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Amino acids as corrosion inhibitors for copper in acidic medium: Experimental and theoretical study•

INGRID MILOŠEV[1]*, JASMINKA PAVLINAC[1]**, MILAN HODOŠČEK[2]
and ANTONIJA LESAR[1]

[1]Jožef Stefan Institute, Department of Physical and Organic Chemistry, Jamova 39, SI-1000, Ljubljana, Slovenia and [2]National Institute of Chemistry, Laboratory for Molecular Modeling, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

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Abstract: Experimental electrochemical methods combined with quantum chemical calculations and molecular dynamics simulations were emplyed to investigate the possibility for the use of various amino acids as "green" corrosion inhibitors for copper in 0.5 M HCl solution. Among the eleven studied amino acids, cysteine achieved the highest inhibitor effectiveness, reaching 52 % at a concentration of 10 mM. The other amino acids achieved an effectiveness of less than 25 %; some of them even acted as corrosion accelerators. Based on the experimental results, the theoretical calculations and simulations were focused on cysteine and alanine. The electronic and reactivity parameters of their protonated forms in an electrical double layer were evaluated by density functional calculations. In addition, molecular dynamic simulations were introduced to follow the adsorption behaviour of these two amino acids at the Cu(111) surface in the electrolyte solution. The results indicate that the orientation of both molecules was nearly parallel to the surface except for the ammonium group, which was directed away from the surface. Therefore, as the orientation of the cysteine and alanine molecules at the surface were similar, the thiol functional group is responsible for the superior inhibition efficiency of cysteine.

Keywords: amino acids; copper; hydrochloric acid; green inhibitors; quantum chemical calculations; molecular dynamics.

INTRODUCTION

Due to their importance in industry and wide range of applications, copper and its alloys have been the subject of numerous investigations since the 1920s.

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* Corresponding author. E-mail: ingrid.milosev@ijs.si
** Present address: Lek d.d.,Verovškova 57, SI-1526 Ljubljana, Slovenia.

• Paper dedicated to Professor Branislav Nikolić.

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These studies aimed at preventing or reducing the corrosion process in aggressive media.[1–10] As corrosion inhibitors, various substances, both inorganic and organic, can be used. While inorganic inhibitors reduce the corrosion through film formation, organic compounds act mostly *via* adsorption processes on the metal surface and complex formation. As most efficient organic corrosion inhibitors could be toxic and thus unacceptable for the environment, contemporary studies are directed towards the search for alternative inhibitors that would be ecologically acceptable, stable, non-toxic and available at a relatively low cost. These compounds, referred to as "green", "eco-friendly", or "environmentally-friendly", comprise both organic and inorganic inhibitors.[9,11–13] Among the organic inhibitors, natural plant extracts are used – from *Aloae vera* to radish leaves; most of them contain hetero-atoms such as N, S, P and O and can thus form protective films.[11–13] Among green inhibitors, studies on lanthanide salts, natural polymers, such as guar gum and starch, and bio-mimicking green inhibitors, such as amino acids, were conducted.[13] Amino acids are completely soluble in aqueous media and can be produced with high purity at low costs.

The majority of the investigations on copper were performed in acidic chloride media (HCl),[14–21] but also in HNO_3,[22,23] H_2SO_4,[24,25] H_3PO_4,[26] and even non-aqueous mineral oil[27] (Table I). Some copper alloys were also investigated, including Cu-5Ni and Cu-65Ni in 0.25 M Na_2SO_4 + 0.05 M H_2SO_4,[28] Cu-30Ni in 0.5 M H_2SO_4,[29] and bronze Cu-3Sn in 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$.[30,31] Among various amino acids, cysteine is the most extensively studied (Table I). This is related to the fact that it contains sulphur, which is expected to beneficially affect the inhibition mechanism, as reported for various organic inhibitors.[4] In HCl solution, cysteine achieved the highest inhibition efficiency (*IE*) of 93 % at 15 mM.[21] Other amino acids were also reported to perform well: alanine 94 % at 1 mM,[14] threonine 83 % and glutamic acid 90 % at 1 mM concentration.[17] Cysteine was also effective in nitric acid.[22,23] Furthermore, cysteine was also effective as a corrosion inhibitor for bronze. It reached an *IE* of 95 % at 10 mM for Cu-3Sn bronze in 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaHCO_3$.[30] For pre-corroded Cu-6Sn samples with bronze disease, a cysteine solution might be a better choice than benzotriazole for long-term exposure in an atmosphere of high relative humidity.[31] In contrast, cysteine was poorly effective as inhibitor for Cu-5Ni and Cu-65Ni alloys in 0.25 M Na_2SO_4 + 0.05 M H_2SO_4.[28] In non-aqueous medium cysteine and histidine were not efficient corrosion inhibitors for Cu.[27]

When comparing various amino acids, their inhibition effect in HCl depended on the type of amino acid and its concentration (Table I). Alanine outperformed aspartic acid and glutamine,[14] glutamic acid was better than serine and threonine,[17] cysteine was better than glycine and glutamic acid,[21] and glutamine was better than glutamic acid, asparagine and aspartic acid.[18] In nitric acid, cysteine

TABLE I. Literature data for the values of the inhibition efficiency (*IE*) for various amino acids as inhibitors of the corrosion of Cu and Cu alloys in different media

Reference	Material, medium	Amino acid	*IE*
14	Cu, 1 M HCl, 25 °C	Alanine	94 % at 1 mM
		Aspartic acid	52 % at 1 mM
		Glutamine	55 % at 1mM
16	Cu, 0.6 M HCl	Cysteine	84 % at 18 mM
		Cysteine + Cu^{2+}	88 % at 18 mM
15	Cu, 0.5 M HCl	Alanine	43 % at 0.01 mM
		Cysteine	59 % at 0.01 mM
17	Cu, 0.5 M HCl	Serine	55 % at 1 mM
		Threonine	83 % at 1mM
		Glutamic acid	90 % at 1mM
20	Cu, 0.5 M HCl	Arginine	63 % at 1 mM
		Arginine + KI	87 % at 1 mM + 5 mM KI
19	Cu, 0.5 M HCl	Methionine	77 % at 12 mM
		Methionine + Zn^{2+}	92 % at 12 mM + 0.5 mM Zn^{2+}
21	Cu, 0.5 M HCl	Glycine	60 % at 15 mM
		Glutamic acid	62 % at 15 mM
		GLY+GLU+CYS	91 % at 15 mM
		Cysteine	93 % at 15 mM
		Glutathione	95 % at 15 mM
18	Cu, 0.5 M HCl	Aspartic acid	57 % at 0.1 M
		Glutamic acid	60 % at 0.1 M
		Asparagine	65 % at 0.1 M
		Glutamine	73 % at 0.1 M
		Glutamine	67 % at 10 mM
		Glutamine + KI	94 % at 10 mM + 5 mM KI
25	Cu, 0.5 M H_2SO_4, 20 °C	Tryptophan	87 % at 10 mM
23	Cu, 1M HNO_3	Cysteine	88 % at 0.1 mM
22	Cu, 0.5 M HNO_3	Valine	–15 % at 1 mM
		Glycine	–4 % at 1 mM
		Arginine	38 % at 1 mM
		Lysine	54 % at 1 mM
		Cysteine	61 % at 1 mM
29	Cu-30Ni, 0.5 M H_2SO_4	Cysteine	91 % at 1mM
30	Cu-3Sn, Na_2SO_4+$NaHCO_3$	Cysteine	95 % at 10 mM
		Alanine	82 % at 1 M
		Phenyl alanine	56 % at 10 mM
28	Cu-5Ni, 0.25 M Na_2SO_4+0.05 M H_2SO_4	Glycine	12 % at 0.05 mM
		Alanine	25 % at 0.1 mM
		Leucine	39 % at 0.01 mM
		Lysine	38 % at 0.2 mM
		Histidine	–3 % at 0.01 mM
		Glutamic acid	38 % at 0.01 mM
		Cysteine	22 % at 0.01 mM

outperformed lysine and arginine.[22] As a corrosion inhibitor for bronze in acidic medium, cysteine was slightly more efficient than alanine and much more efficient than phenyl alanine.[30]

The inhibition efficiency of amino acids was improved by the addition of anions, such as iodide, and cations, such as Zn^{2+} and Cu^{2+}.[19,20] The synergistic effect of iodide ions was ascribed to a strong chemisorption of the ions on the metal surface. The columbic attraction between the chemisorbed anion and the cation of an amino acid leads to greater surface coverage and hence, greater inhibition efficiency.[19,20] The synergistic effect of Cu^{2+} was ascribed to the formation of a copper cysteinate complex (Cu(I) cysteine).[16] The Cu^+ formed by the reduction of Cu^{2+} react with cysteine to form the Cu(I) cysteine complex which deposit at the surface and inhibits the cathodic partial reaction. A similar effect was reported for methionine in the presence of Zn^{2+}.[19]

In order to reveal the adsorption mechanism, different adsorption isotherms were tested.[14,16,17,19,25,26] Taking into account a commonly accepted value of $–40$ kJ mol$^{–1}$ as a threshold between chemisorption and physisorption, the collected data indicated that the operative mechanism of adsorption of amino acids to a copper surface is physisorption.

Amino acids generally act as cathodic inhibitors, *i.e.*, they inhibit the cathodic partial reaction to a larger extent than the anodic partial reaction.[14–16,18,22,24,29,30] With increasing concentration of amino acid, the inhibition efficiency generally increased,[18,21,29] although deviations from this behaviour have been observed.[16,28,30] At a given concentration, the degree of protection decreased with temperature in the range from 25 to 55 °C.[14] The value of *IE* was noticed to increase with time of immersion.[20] An accelerating effect of some amino acids (glycine, alanine, leucine, lysine, histidine, glutamic acid and cysteine) on the corrosion was observed for the Cu–5Ni alloy in HCl solution,[28] and valine and glycine for Cu in nitric acid.[22]

The aim of the present work was to study several amino acids as corrosion inhibitors of copper corrosion in hydrochloric acid. The experimental electrochemical studies were supplemented with a theoretical investigation based on quantum chemical methods to characterize the electronic and reactivity parameters, while molecular dynamics simulations were applied to describe the adsorption behaviour of amino acid inhibitors in the electrolyte solutions at the molecular level. In this work, the investigations were focused on cysteine (CYS) and alanine (ALA) amino acids. Cysteine could be considered as alanine derivative in which one of the hydrogen atom of the terminal $–CH_3$ group of alanine is substituted by a –SH functional group.

EXPERIMENTAL

Amino acids

Eleven of the standard twenty α-amino acids were tested. The Lewis structures, names and abbreviations of the amino acids used in this study are summarized in Fig. 1. Amino acids can be generally sorted into six main groups based on their structure and the chemical characteristics of their functional (R) groups: aliphatic, hydroxyl- or sulphur-containing, cyclic, aromatic, basic and acidic. In the present work the following groups were tested regarding the functional group, polarity, charge and sulphur-containing group (Fig. 1):

Group I: aliphatic, non-polar, neutral amino acids: glycine (GLY), alanine (ALA), leucine (LEU) and methionine (MET); among these, methionine is S-containing;

Group II: uncharged group, non-polar, neutral amino acids: threonine (THR), asparagine (ASN) and cysteine (CYS); among these the cysteine is S-containing;

Group III: charged group, polar and basic amino acids: histidine (HIS) and arginine (ARG);

Group IV: aromatic, non-polar, neutral amino acids: tryptophan (TRP) and tyrosine (TYR).

All tested amino acids are L-enantiomers, except for glycine which is without a centre of chirality. Methionine and cysteine are the only ones to contain sulphur. Histidine and arginine

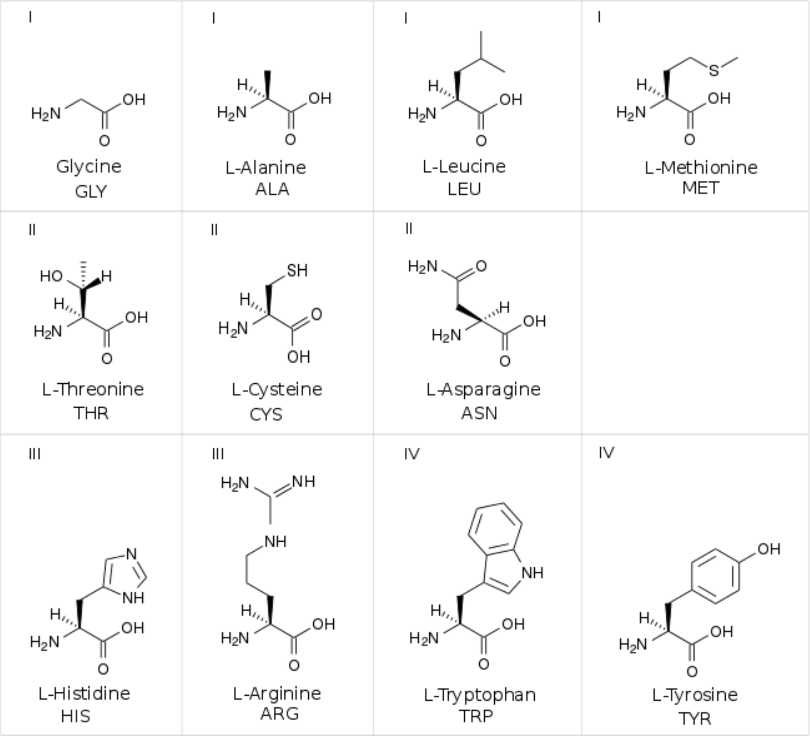

Fig. 1. Lewis structures, names and abbreviations of the amino acids. Roman number in the left corner denotes the group of the amino acids: I) aliphatic group, non-polar, neutral, II) uncharged group, polar, neutral, III) charged group, polar, basic and IV) aromatic group, non-polar, neutral.

are charged polar basic acids, whilst tryptophan and tyrosine belong to aromatic acids. Among these eleven amino acids, four are classified as essential: leucine, methionine, threonine and tryptophan.

The structure of the amino acids are sensitive to the phase, the different forms of the amino acids depending on the medium are displayed in Fig. 2. At pH between 2.2 and 9.4 (mean values for 20 common amino acids), the predominant form adopted by α-amino acid contains a negative carboxylate and a positive ammonium group, so has net zero charge (zwitterion form). Since amino acids have slightly different acid dissociation constants, (pK_a values), their iso-electric points, pI, are different (pI = 1/2(pK_{a1} + pK_{a2}).[32] Below 2.2 and above 9.4, the net charge is positive and negative, respectively. In acidic medium, they result from –the protonation of NH_2 group ($–NH_3^+$), while in alkaline medium, the –COOH group is deprotonated ($–CO_2^-$).

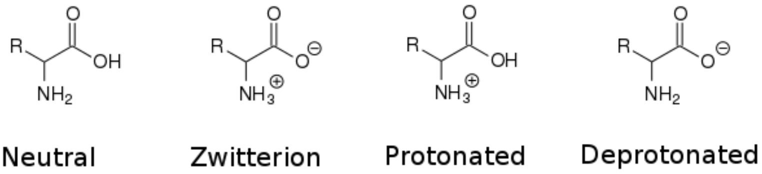

Fig. 2. The scheme of the amino acid forms depending on the medium.

Electrochemical measurements

Copper (99.9 %) was supplied by Goodfellow (Cambridge Ltd., UK) as 2-mm thick foil Samples were cut in the shape of discs of 15 mm in diameter. Prior to the measurements, the samples were mechanically ground under water using SiC paper successively up to 4,000-grit to achieve a surface with a uniform pattern of scratches. The samples were cleaned with ethanol in an ultrasonic bath for two minutes, double-rinsed with double-distilled water, and finally dried in a stream of nitrogen.

Electrochemical measurements were realised in a three-electrode corrosion cell (volume 350 mL) at room temperature. A specimen embedded in a Teflon holder, with an area of 0.785 cm^2 exposed to the solution, served as the working electrode. A saturated calomel electrode (SCE, 0.2415 V *vs*. saturated hydrogen electrode, SHE) was used as the reference electrode and carbon rods as the counter-electrode. Electrochemical experiments were realised using a PAR & EGG 263A potentiostat/galvanostat and controlled by Powersuite software. The measurements were performed in an aerated 0.5 M HCl (37 %) solution (Carlo Erba Reagents, Rodano, Italy). The amino acids were added to the HCl solution at a concentration of 10 mM.

Prior to the measurements, the samples were allowed to stabilize for 1 h under the conditions of the open circuit potential, E_{oc}. Potentiodynamic measurements were performed using a 1 mV s^{-1} potential scan rate, starting at 250 mV negative to the stabilized E_{oc} and then increased in the anodic direction. The values of E_{corr} and j_{corr} were determined from Tafel analysis. For each sample, measurements were performed at least in duplicate. Representative polarization curves were selected for graphical presentations. The inhibition effectiveness, *IE*, was calculated according to the formula:

$$IE = 100\frac{j_{corr,inh} - j_{corr}}{j_{corr,inh}} \quad (1)$$

where $j_{\mathrm{corr,inh}}$ and j_{corr} are the corrosion current density in the inhibited and uninhibited solution, respectively.

Quantum chemical calculations

The molecular behaviour of cysteine (CYS) and alanine (ALA) as corrosion inhibitors for copper metal in acidic medium was studied by the quantum electrochemical approach. Density functional theory, specifically the B3LYP functional[33-35] using flexible 6-311G** basis set[36] containing polarization and diffuse functions, was used for the calculations of the electronic structure and reactivity parameter. Frequency calculations for species were calculated to verify the minimum-energy structures. Special care was devoted to setting up a reliable model that accounted for the experiment conditions. The corrosion process occurs in the liquid phase, thus, the self-consistent reaction field (SCRF) theory,[37] with the Tomasi polarized continuum model (PCM),[38] was used to perform the calculations in solution. These methods model the solvent as a continuum of uniform dielectric constant ($\varepsilon = 78.5$) and define the cavity where the solute is placed as a uniform series of interlocking atomic spheres. While the inhibitory action does not occur in the bulk solution but is related to the electrical double layer (EDL) interface, *i.e.*, the molecule–solution interface, a dielectric constant of 6.0 is more appropriate.[39] While an electric field is present in the EDL, it seems reasonable to check the effect of the EDF electric field, which was considered as a finite electric field (10^7 V cm^{-1}) along the dipole moment of molecule included in the Hamiltonian. Under these conditions, the electronic parameters, such as HOMO–LUMO energy gap and dipole moment, were calculated for CYS and ALA inhibitor molecules. Furthermore, the following global reactivity parameters: electronic chemical potential, global chemical hardness and the fraction of transferred electron were evaluated. The local reactivity parameters were analysed by means of Fukui indices,[40] calculated by the finite difference approximation approach.[41] The details of these calculations are widely available elsewhere.[42] The Gaussian 09 program package[43] was used for all quantum chemical calculations.

Molecular dynamics studies

Molecular dynamic simulations were applied to evaluate the interaction of the amino acid molecules with the cooper surface in acid solutions. The surface of Cu(111) was chosen to investigate the orientation and dynamics of CYS and ALA in electrolyte solutions. Cu atoms were restrained with a force constant of 50 kcal mol^{-1} Å^{-3} throughout the simulation. The model of the solution was set up in a way to correspond a solution of 10 mM CYS (ALA) in an aqueous 0.5 M HCl solution. Two all-atom models were generated to summarize the experimental conditions. The model related to CYS in HCl medium illustrates the protonated form (CYS-PH), and also for ALA in HCl media, the protonated form (ALA-PH) is operative. Setting up the corresponding concentrations of experimental HCl electrolyte solution, 5000 water molecules were included in the orthorhombic box with the sizes 56.1, 53.1, 52.0 Å and then one molecule of amino acid was randomly added into the box. Furthermore, 45 protons randomly coupled with H_2O molecules to form H_3O^+ were added and the same number of chlorine anions. At constant pressure (1 atm) and temperature (300 K), the molecular dynamics protocol was applied in the equilibration phase of 100 ps. Then 20 ns long trajectory of the system with step-size of 1 fs and 3D periodic boundary conditions were pursued. The CHARMM program package[44] was employed for the molecular dynamics simulations using CHARMM version 36 parameter set[45] for the amino acids and ions. Parameters for copper atoms were produced according to the CHARMM parameter set development standard using *ab initio* results from a water molecule on a Cu(111) surface.[46]

RESULTS AND DISCUSSION

Potentiodynamic curves in hydrochloric acid with and without the addition of amino acids

The electrochemical behaviour of copper in 0.5 M HCl has been extensively studied.[1] A polarization curve is presented in Fig. 3. In HCl solution, the mechanism of cathodic reaction in the vicinity of the corrosion potential involves the reduction of dissolved oxygen:[1]

$$O_2 + 4H^+ + 4e^- \leftrightarrows 2H_2O \qquad (2)$$

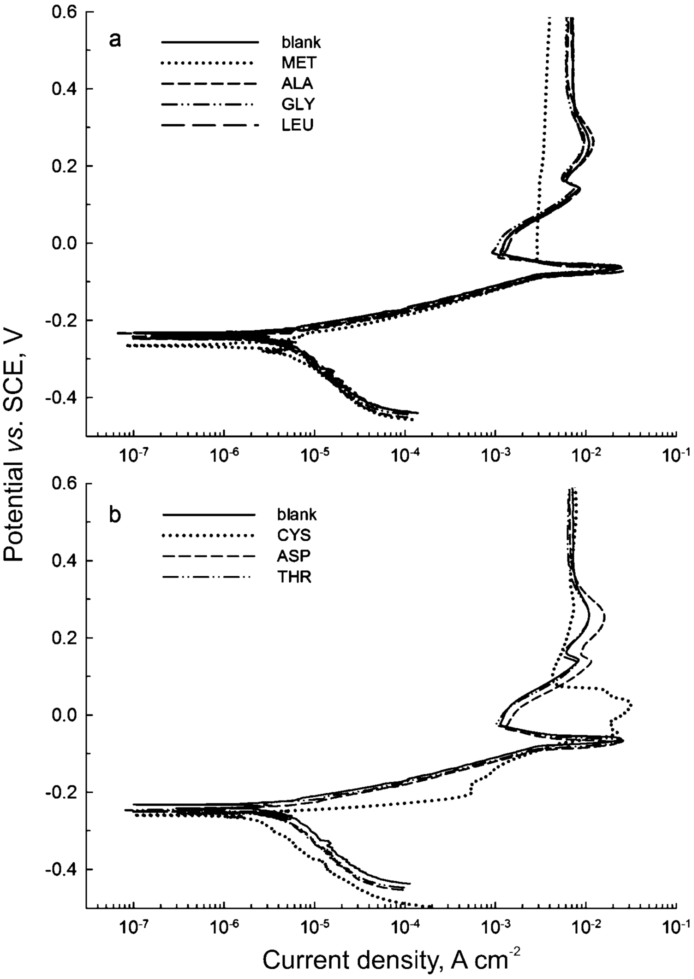

Fig. 3. Potentiodynamic polarization curves recorded for Cu in blank 0.5 M HCl and in 0.5 M HCl containing 10 mM of amino acids from a) group I: glycine (GLY), alanine (ALA), leucine (LEU) and methionine (MET) and b) group II; threonine (THR), asparagine (ASP) and cysteine (CYS). d*E*/d*t* = 1 mV s^{-1}.

The anodic curve shows three distinct regions: active dissolution in the apparent Tafel region, a transition region with the maximum current density and the limiting current region. It was proposed that $CuCl_2^-$ complex may be formed either through direct formation from the metal:

$$Cu + 2Cl^- \leftrightarrows CuCl_2^- + e^- \tag{3}$$

or

$$Cu + Cl^- \leftrightarrows CuCl + e^- \tag{4}$$

$$CuCl + Cl^- \leftrightarrows CuCl_2^- \tag{5}$$

The dissolution may also include dissolution of copper as the Cu^+ in the first instance:[1]

$$Cu \leftrightarrows Cu^+ + e^- \tag{6}$$

$$Cu^+ + 2Cl^- \leftrightarrows CuCl_2^- \tag{7}$$

In the apparent Tafel region, mixed charged transfer and mass transport are usually assumed.[1] The reaction is controlled by both electro-dissolution of copper and diffusion of $CuCl_2^-$ to the bulk solution.[1] The linear slope close to 60 mV denotes a one-electron transfer reaction. Film formation is reflected in the peak at –0.07 V followed by a decrease in the current density (Fig. 1). At the current minimum, the surface CuCl coverage reached its maximum. However, CuCl species do not attain sufficient protection since, due to film dissolution, reaction (5), or metal dissolution, reaction (7), the current density progressively increases. The cuprous chloride complex can further dissolve according to:

$$CuCl_{2,ads}^- \leftrightarrows Cu^{2+} + 2Cl^- + e^- \tag{8}$$

This process denotes the establishment of the limiting current region at approximately 0.4 V and continues at more positive potentials. Thus, the overall reaction for copper corrosion can be represented by:

$$2Cu + 4H^+ + 4Cl^- + O_2 \rightarrow 2Cu^{2+} + 4Cl^- + 2H_2O \tag{9}$$

Polarization curves recorded in the presence of amino acids are generally similar to blank curve (Figs. 3 and 4). Depending on the type of amino acid, its effect on the corrosion process of Cu can be accelerating (increasing the j_{corr} value) or inhibitory (decreasing the j_{corr} value), accompanied by the corresponding shift of the E_{oc} and E_{corr} values. The resulting inhibition effectiveness, *IE*, and values of E_{oc} and E_{corr} are presented in Fig. 5. Among the aliphatic amino acids, alanine and leucine modestly accelerated the corrosion process (*IE* of –12 and –2 %, respectively), whilst glycine had an almost negligible inhibitory effect. A slightly higher effect, but still modest, was achieved by methionine which exhibited a shift in E_{corr} to 30 mV more negative values and the smallest current density of the cathodic branch (Fig. 3a). In the anodic part, the differences were almost negligible compared to the blank curve. At potentials more positive than the anodic peak, the curve for methionine differed from those of the other amino acids; it formed a current density plateau over a broad potential range.

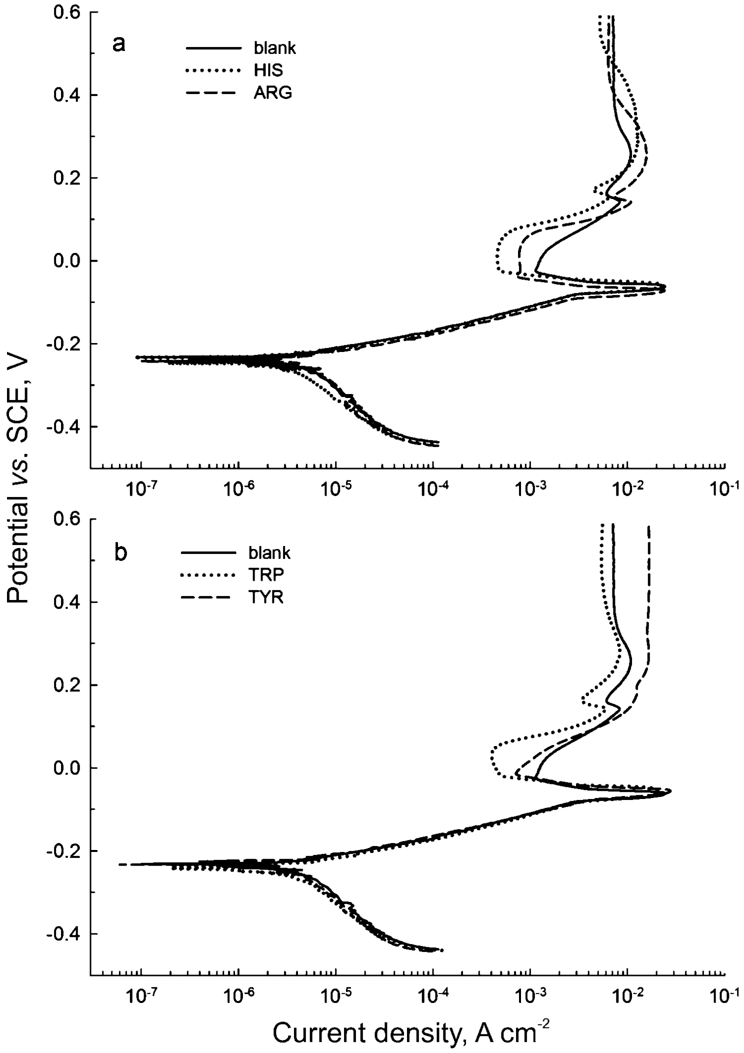

Fig. 4. Potentiodynamic polarization curves recorded for Cu in blank 0.5 M HCl and in 0.5 M HCl containing 10 mM of amino acids from a) group III: histidine (HIS) and arginine (ARG), and b) group (IV): tryptophan (TRP) and tyrosine (TYR). dE/dt = 1 mV s^{-1}.

Polar, neutral amino acids exhibited the most distinguished differences compared to the blank curve in the cathodic part (Fig. 3b): the cathodic current density decreased by approximately half a decade and the corrosion potential shifted in negative direction by 10–30 mV. In terms of *IE*, asparagine produced no effect, threonine achieved a value similar to that of methionine, 12 %, whilst the *IE* for cysteine was 52 % (Fig. 5a). In the anodic branch, the current densities for asparagine and threonine were slightly higher compared to the blank, whilst for cysteine, a small peak was formed at around –0.2 V. At more positive potentials, in addition to the peak at –0.07 V, ascribed to CuCl formation, another peak formed at 0.01 V, followed by a decrease in the current density and a limiting plateau region. Among the examined amino acids, the formation of two additional anodic peaks, at –0.2 and 0.01 V, was unique for cysteine.

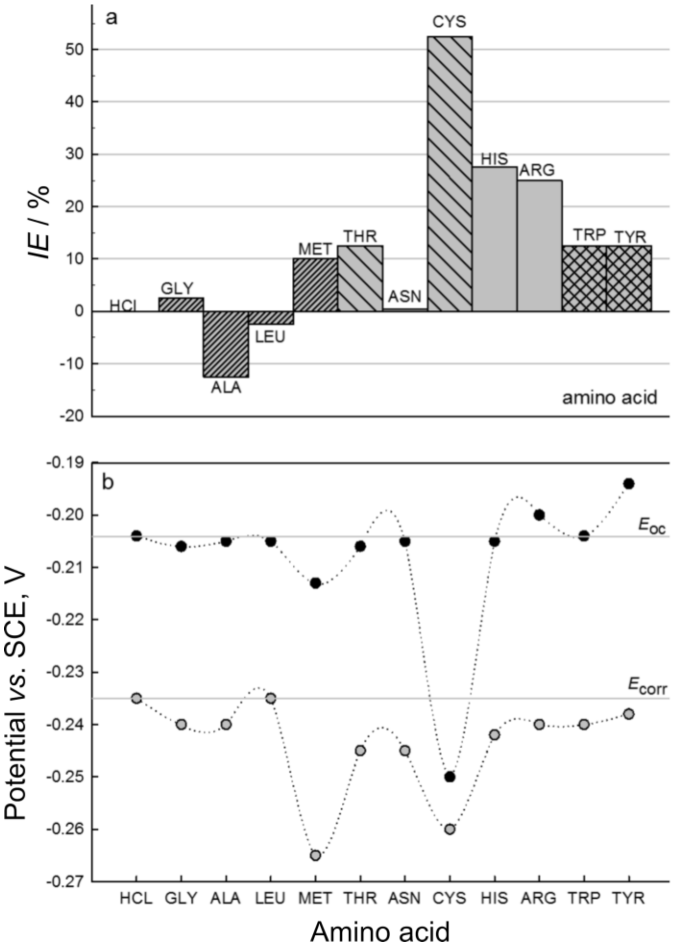

Fig. 5. a) Inhibition effectiveness, *IE*, deduced for copper from the values of the corrosion current density measured in 0.5 M HCl solution inhibited by various amino acids. b) Values of the open circuit potential, E_{oc}, and corrosion potential, E_{corr}, measured for copper in 0.5 M HCl solution inhibited by various amino acids.

Among the basic, non-polar amino acids, histidine and arginine with imidazole and guanidinium functional groups, histidine exhibited smaller current densities in the cathodic part (Fig. 4a). The *IE* values of 27 and 25 % were larger than those for aliphatic amino acids, but smaller than that for cysteine (Fig. 5a). In the region following the anodic peak, both amino acids caused a decrease in the current density. A plateau of ≈50 mV was established, which was not the case in the blank solution or in the presence of aliphatic and polar, neutral amino acids. The aromatic amino acids tryptophane and tyrosine showed similar behaviour: at potentials less negative than the anodic peak, only slight differences occurred compared to the blank curve (Fig. 4b). The resulting *IE* value for both was 12 % (Fig. 5a). In the region following the anodic peak, at ≈0 V, the related current density was smaller in the presence of tyrosine and, especially, of tryptophan, which formed a plateau of 40 mV.

Inhibition effectiveness of the amino acids

Two amino acids, alanine and leucine, slightly accelerated the corrosion process (Fig. 5a). No effect was observed for asparagine. All other amino acids acted as corrosion inhibitors, with cysteine being the most effective with an *IE* value of 52 %. The following order was observed: CYS > HIS ≈ ARG > THR ≈ TYR ≈ ≈ TRP > MET > GLY.

It is noteworthy that the difference in the effect of cysteine and methionine was quite large (Fig. 5a) although both contain sulphur which is believed to be mainly responsible for the strong adsorption of organic molecules. The adsorption achieved through thiol (S–H) group of cysteine was obviously stronger than through the methylthio ($S–CH_3$) group of methionine (Fig. 1). Furthermore, cysteine acted as an inhibitor and alanine as an accelerator although they differ only in the presence of the thiol group.

The values of open circuit potential, E_{oc}, measured after 1 h immersion and corrosion potential, E_{corr}, determined by Tafel analysis for the blank HCl solution and in the presence of various amino acids, are presented in Fig. 5b. Cysteine showed the most negative shift of E_{oc} followed by methionine, while the other amino acids showed very similar values to the blank. Among the E_{corr} values, methionine and cysteine again shifted them to the most negative values, compared to the blank.

Quantum chemical results

Two amino acids, cysteine and alanine, were considered. Cysteine achieved best inhibition effectiveness; on the other hand, alanine acted as corrosion accelerator; these two amino acids differ only in the presence of a thiol group (Fig. 1). The calculations have been adjusted to the experimental conditions as much as possible, *i.e.*, amino acids were considered in the protonated forms denoted as

CYS-PH and ALA-PH. The electronic data have been calculated with the model of inhibitors in EDL and with the model of inhibitors in EDL applying a finite electric field in the *z*-direction. The EDL has been simulated with solvent dielectric constant of 6.0 and the electric field of 10^7 V cm^{-1} has been applied. The B3LYP/6-311G** fully optimized structures of protonated forms of CYS and ALA molecules calculated for the EDL model are displayed in Fig. 6, where the most relevant bond distances are also stated. The bond distances calculated for the model with external field are insignificantly different from those given in the figure. The inhibitor performance was analysed by quantum chemical parameters responsible for the inhibitory action and was further addressed by evaluating the global reactivity parameters. Table II presents the HOMO–LUMO energy gap (ΔE) and dipole moment as electronic parameters and the following reactivity parameters: electronic chemical potential (μ), global chemical hardness (η) and the fraction of transferred electron (ΔN). The calculated values for both models employed are quite similar implying that the external field has small influence on the electronic as well as on the reactivity parameters of studied amino acids. Low values of energy gap are associated with effective inhibition. The ΔE results support the better inhibition effectiveness of cysteine in acid media compared to alanine. Further, similar conclusions are confirmed by the results on electronic chemical potential and global chemical hardness.

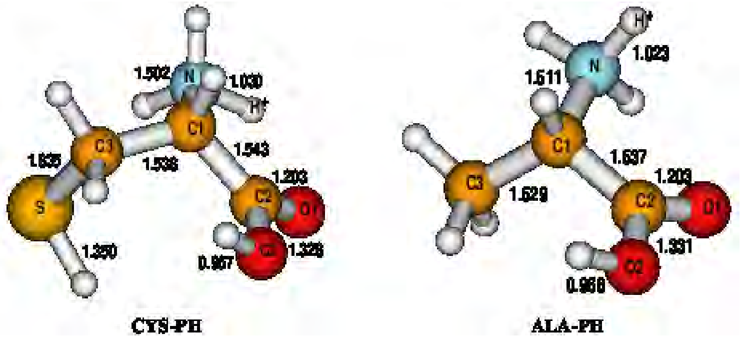

Fig. 6. The equilibrium structures (selected B3LYP/6-311G** bond distances in Å) of the protonated forms of cysteine and alanine molecules in the EDL molecule–aqueous solution interface.

To examine the local reactivity behaviour we have calculated the Fukui indices, which are summarised in Table III. The atomic sites with the maximum value of f_i^- are the preferred sites to which the amino acid molecule will donate charge when attacked by an electrophilic reagent. On the other hand, a large value of f_i^+ is assigned to the atomic sites where the amino acid molecule will receive charge, when attacked by a nucleophilic reagent. In the acid medium, the S atom of cysteine molecule is the most favourable site for an electrophilic attack. For CYS-PH C2 and O1 are the preferred sites for nucleophilic attack. On the other hand, O2 and O1 atoms of ALA-PH are the most reactive centres for an electrophilic attack. C2 and O1 atoms participate in the nucleophilic attack of ALA-PH. From Fukui analysis it can be concluded that more centres are involved in the adsorption process of the both amino acid molecules.

TABLE II. Electronic parameters (HOMO–LUMO energy gap (ΔE), dipole moment) and global reactivity parameters (electronic chemical potential (μ), global chemical hardness (η), the fraction of transferred electron (ΔN)) of protonated cysteine and alanine forms in acidic medium; a: $\varepsilon = 6.0$; b: $\varepsilon = 6.0$, with an electric field of 10^7 V cm^{-1}

Species	Model	ΔE / eV	Dipole moment, Debye	μ	η	ΔN
CYS-PH	a	6.44	7.40	–5.04	3.22	–0.01
	b	6.40	6.89	–5.04	3.22	–0.01
ALA-PH	a	7.85	8.70	–5.48	3.93	–0.06
	b	7.81	8.97	–5.52	3.91	–0.07

TABLE III. Condensed Fukui functions (f^-, f^+) of protonated cysteine and alanine forms in acidic medium. The most favourable sites for electrophilic and nucleophilic attacks are bold; a: $\varepsilon = 6.0$; b: $\varepsilon = 6.0$, with an electric field of 10^7 V cm^{-1}

Species		Model	C1	C2	N	O1	O2	C3	S
CYS-PH	f^-	a	0.00	0.02	–0.01	–0.04	–0.02	0.04	**–0.80**
		b	0.00	0.01	–0.01	–0.04	–0.02	0.04	**–0.80**
	f^+	a	0.00	**–0.19**	–0.01	**–0.14**	–0.06	0.00	–0.10
		b	–0.01	**–0.17**	–0.02	**–0.13**	–0.06	0.00	–0.08
ALA-PH	f^-	a	–0.06	0.00	0.00	**–0.54**	**–0.13**	–0.01	–
		b	–0.06	0.00	0.00	**–0.54**	**–0.13**	–0.01	–
	f^+	a	0.00	**–0.16**	–0.02	**–0.13**	–0.06	0.00	–
		b	–0.03	**–0.22**	–0.06	**–0.14**	–0.07	0.01	–

Molecular dynamics results

The adsorption structures of CYS and ALA amino acids at the Cu(111) surface in the acid medium provided by molecular dynamics simulations were analysed through graphical visualization of the adsorption configurations in the electrolyte solution. The result of simulations of both models are shown in Fig. 7, where on left panel snapshot configurations of corresponding form of CYS or ALA after 20 ns dynamic simulations are displayed, while on right panel normalized histograms of the atomic positions perpendicular to the Cu(111) surface (Cu atoms being at 0 position) for the selected atoms of amino acid molecule forms are summarized. From top right panel in Fig. 7, it can be easily seen that the distances of the S, O1, O2 and C3 atoms of CYS-HP from the Cu surface are nearly the same; for the S atom the distance amounts to 2.3 Å. The distance of N atom from the Cu surface is in the range 3.7–4.1 Å, implying that the protonated cysteine molecule is absorbed nearly parallel to the copper surface, but with $–NH_3^+$ group oriented away from the surface into the solution. Furthermore, it could be concluded from the figure that the protons are distributed throughout the solution and approach not less than 2.0 Å to the surface. Moreover, chlorine anions are distributed throughout the solution with minimum distance to the surface of 2.7 Å.

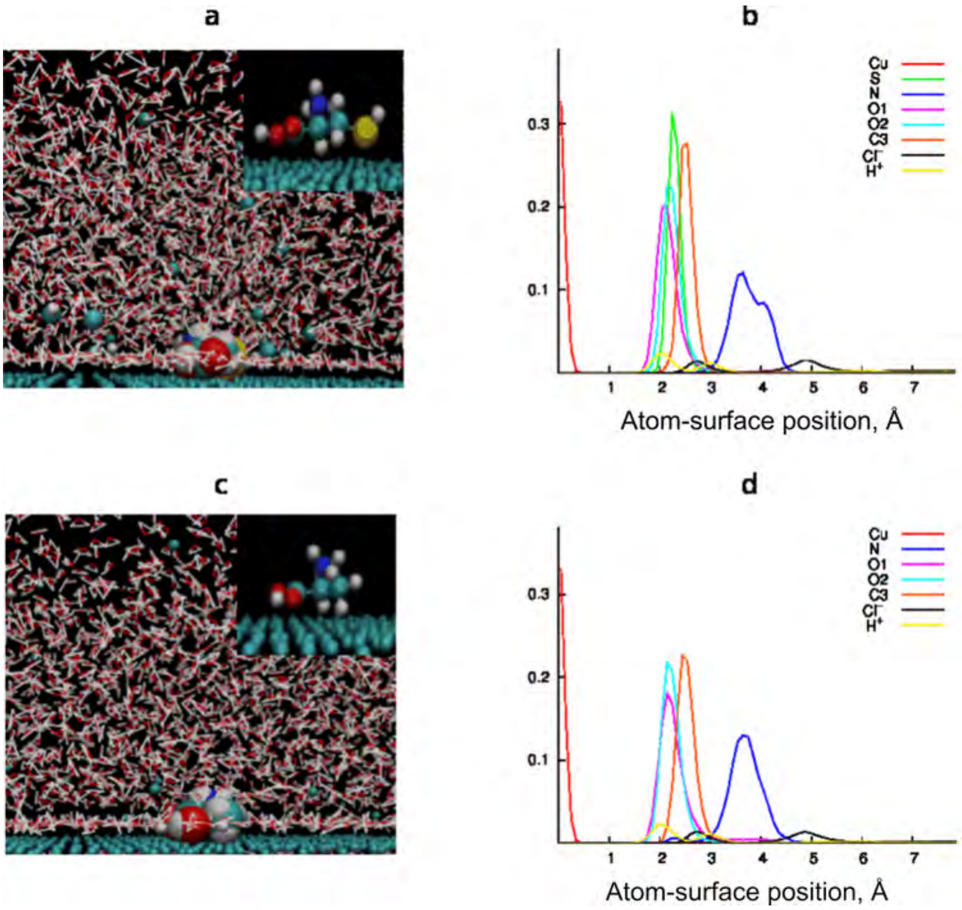

Fig. 7. Adsorption configurations (a and c panel) and normalized histograms of atomic positions relative to Cu(111) surface (b and d panel) for cysteine and alanine molecules in acid medium. In insets the medium is excluded to present more clearly the adsorption configurations of molecules at the Cu(111) surface (green). Legend: amino acid: O (red), N (blue), S (yellow), C (green), H (grey); medium: H_2O (white), H_3O^+ (red), Cl (green).

The ALA molecule in HCl electrolyte solution is shown in panels c and d of Fig. 7. Compared to the protonated form of cysteine, similar conclusions were drawn for orientation of protonated alanine molecule in acid solution. The only noticeable small difference is more sharp position of N atom with the maximum at 3.7 Å above the Cu surface. It should be mentioned that an S atom is not involved in this amino acid.

CONCLUSIONS

An experimental electrochemical and a theoretical study were performed to investigate the possibility of employing various amino acids as corrosion inhibitors for copper in 0.5 M HCl solution. Eleven tested amino acids were divided into four groups based on the type of functional group, polarity, charge and presence of sulphur. No clear relationship between the groups was noticed in terms of the inhibition effectiveness in hydrochloric acid, *i.e.*, amino acids from the same group may act as corrosion inhibitor or corrosion accelerator. The experimental results confirmed that cysteine exhibited the largest inhibition effectiveness reaching about 50 % at a concentration of 10 mM. Histidine and arginine reached *IE* values of about 25 %, while the other amino acids yielded only moderate effects, not important for practical use. Alanine and leucine acted as corrosion accelerators.

The reasons for diametrically opposed behaviour of cysteine and alanine, differing only in the presence of a thiol group, were investigated further using quantum chemical calculations and molecular dynamics simulations. The better inhibition effectiveness of cysteine compared to alanine was confirmed by the results of the HOMO–LUMO energy gap, electronic chemical potential and global chemical hardness. The calculated local reactivity parameters indicated that several atomic centres are involved in the adsorption process of both amino acid molecules. The electrophilic attack of cysteine molecule is strongly related to the S atom, while in alanine molecule, both the O1 and O2 atoms are the favourable sites. On the other hand, C2 and O1 are preferred sites for nucleophilic attack, in other words, the –C=O carbonyl group is operative in a back donation process. The molecular dynamics simulations provided a relative comparison of the orientation of cysteine and alanine inhibitors in 0.5 M HCl solutions at the Cu(111) surface. No significant difference could be observed for the absorption of these amino acids regarding their orientation at the metal surface. Yet, cysteine achieved high inhibition effectiveness which can be ascribed to adsorption through the thiol group. Finally, the results of global reactivity parameters and those of molecular dynamic simulations do not support the participation of N atom of ammonium group in the adsorption process.

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ИЗВОД

АМИНОКИСЕЛИНЕ КАО КОРОЗИОНИ ИНХИБИТОРИ ЗА БАКАР У КИСЕЛОЈ СРЕДИНИ: ЕКСПЕРИМЕНТАЛНА И ТЕОРИЈСКА СТУДИЈА

INGRID MILOŠEV[1], JASMINKA PAVLINAC[1], MILAN HODOŠČEK[2] и ANTONIJA LESAR[1]

[1]*Jožef Stefan Institute, Department of Physical and Organic Chemistry, Jamova 39, SI-1000, Ljubljana, Slovenia* и [2]*National Institute of Chemistry, Laboratory for Molecular Modeling, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*

Коришћењем експерименталних електрохемијских метода у комбинацији са квантно-хемијским израчунавањем и симулацијама молекуларне динамике проучаване су могућности употребе различитих аминокиселина као “зелених” корозионих инхибитора за бакар у 0,5 M раствору HCl. Између једанаест тестираних аминокиселина цистеин је показао најбољу корозиону заштиту (52 % при концентрацији 10 mM). Остале аминокиселине су постигле заштиту мању од 25 %; неке међу њима чак делују као акцелератори корозије. На основу добијених експерименталних резултата за теоријска израчунавања и симулације изабрани су цистеин и аланин. Електронски и реактивни параметри електрохемијског двослоја одређени су за протоноване облике аминокиселина помоћу рачунања на основу теорије функционала густине. Симулацијом молекуларне динамике праћена је адсорпција ових аминокиселина на Cu(111) равни у раствору електролита. Оријентација обе аминокиселине је скоро паралелна са површином са изузетком амонијум групе која је усмерена од површине. Будући да је оријентација цистеина и аланина на површини слична, може да се закључи да је тиолска група у цистеину одговорна за његову супериорну корозиону заштиту у односу на друге аминокиселине.

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