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The Effect of Cysteine on the Behaviour of Copper in Neutral and Alkaline Sulphate Solutions

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The behavior of copper in the presence of cysteine in the concentration range $1 \cdot 10^{-6}$ M - $1 \cdot 10^{-2}$ M in a 0.5 M Na_2SO_4 solution (pH 7 and pH 9) is studied using potentiodynamic polarization and chronoamperometry. Potentiodynamic polarization shows that cysteine acts as a copper corrosion inhibitor both in alkaline and neutral sulphate solutions. The inhibitory action occurs through $Cu(I)_{ads}$, which participates in the formation of the Cu(I)-cys film on the metal surface. At higher anodic potentials $Cu(II)_{ads}$ occurs, which is unfavourable for the adsorption of cysteine. The efficiency of corrosion inhibition increases as cysteine concentration increases. Chronoamperometry results are in accordance with the results of potentiodynamic polarization. The adsorption of cysteine proceeds according to the Langmuir adsorption isotherm.

Keywords: copper, cysteine, sulphate, corrosion, polarization.

1. INTRODUCTION

Copper and its alloys have a wide range of applications in many branches of industry owing to their superior properties. However, numerous literature data indicate that under certain conditions they may become susceptible to corrosion [1, 2]. Generally, passivation occurs in alkaline medium as a result of copper oxide formation [3], but in the presence of sulphate ions corrosion occurs frequently in the form of pitting [4]. This problem has initiated a lot of scientific research on corrosion prevention and a significant number of potential corrosion inhibitors have been investigated [5, 6]. Earlier research has shown that benzotriazole has an important application and proved to be an efficient corrosion inhibitor for copper and its alloys in alkaline media [7 - 11] as well as in alkaline media containing sulphate ions [12]. The inhibitory effect in sulphate solutions has also been established for bis-[4H-5 hydroxy-1,2,4-triazol-3-yl]methane (BHTAM) [13], purine and adenine [14 - 16]. Due to the fact that many compounds used as corrosion inhibitors have certain undesirable properties like toxicity, more attention has been devoted lately to discovering non-toxic ecological inhibitors. Amino acids, being available and non-toxic compounds that are easily produced, are therefore interesting as potential corrosion inhibitors for copper and its alloys. The reaction mechanism of amino acids as metal corrosion inhibitors involves adsorption on metal surface [17,18]. Having that in mind, the presence of aromatic ring and heteroatom, such as sulphur and nitrogen, in the structure of aminoacid was found to considerably increase inhibition efficiency [17, 19 - 21]. In particular, amino acids containing sulphur have shown superior inhibition efficiency attributed to the presence of sulphur atoms as a result of which they can be adsorbed as bidentate ligands with coordination taking place through amino or carboxyl group and –SH [20, 22 - 25]. One of them is cysteine whose structure is shown in Fig. 1.

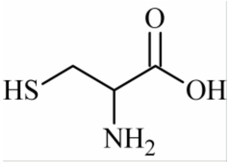


Figure 1. Cysteine structure

As far as the influence of pH is concerned [26], it can be said that at isoelectric point amino acids are in the zwitterion form (Fig. 2a), in alkaline medium, they take the form of anion (Fig. 2b), whereas in acid medium, they are in the cation form (Fig. 2c).

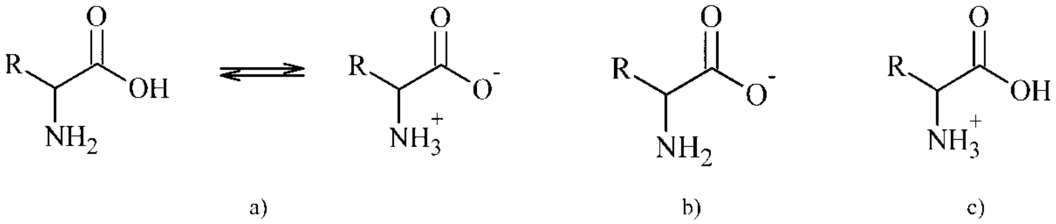

a) b) c)

Figure 2. The form of amino acid depending on the pH value of the medium

Depending on the pH value of the medium, the percentage of the dominant form of amino acid varies. Quantum mechanics calculations done by Bereket and Yurt [26] using PCMODEL show that dipole moment values follow the order anion > cation > zwitterion. At pH close to isoelectric point,the inhibition effect is minimal, whereas in alkaline medium the dipole moment is higher and the inhibition is stronger. The zwitterion structure of cysteine is dominant inthe pH range from 1.91 to 8.16, whereas above and below these values cation and anion forms are dominant, respectively [27, 28]. Cysteine was found to be a good inhibitor of copper corrosion in HCl solutions [21, 23], NaCl [23], nitric acid [20] and sulphuric acid [28] solutions. However, the effect of cysteine on copper behaviour in neutral and alkaline sulphate solutions has not been investigated hitherto. On the basis of the previously shown influence of pH on the form of cysteine molecule and the results of investigation conducted by El-Rabiee et al. [18] showing that amino acids act as metal corrosion inhibitors in neutral and alkaline media, it could be assumed that cysteine wouldalsoact as copper corrosion inhibitor in these media. The behaviour of brass in neutral and alkaline sulphate media containing cysteine was studied recently by Radovanović et al. [29] and its effect as inhibitor of corrosion was confirmed. The experiments were carried out in 0.5 M Na_2SO_4 solutions of pH 7 and 9 and with the addition of varying quantities of cysteine so that concentrations ranged from $1\cdot10^{-6}$ M to $1\cdot10^{-2}$ M. The behaviour of copper in these solutions was investigated by determining the opencircuit potential by means of potentiodynamic and potentiostatic polarization. Changes in the electrode surface conditions were being observed. After the measurements were performed, the electrode surface was observed under the microscope and the photographs were taken.

2. EXPERIMENTAL

2.1. Electrode preparation

The working electrode was made of copper wire obtained by upcasting procedure. It was prepared by cutting wire and cold sealing it with a material based on methyl-metacrylate. The working area of Cu electrode was 0.49 cm^2. Prior to each measurement the Cu electrode was polished using 0.3 μm grit alumina paste (Al_2O_3), then rinsed with distilled water and dried. The reference electrode was a saturated calomel electrode (SCE), whereas the auxiliary electrode was made of platinum.

2.2. Reagents

The following solutions were used: 0.5 M Na_2SO_4 (Zorka Šabac) as the basic solution whereby the pH value of the solution was regulated by adding NaOH (Zorka Šabac). The solutions having pH ~ 7 and pH ~ 9 were used. Cysteine (Merck) was added directly into the solution of sodium sulphate to obtain a $1\cdot10^{-2}$ M solution which was further diluted giving a series of solutions whose concentration were $1\cdot10^{-3}$ M; $1\cdot10^{-4}$ M; $1\cdot10^{-5}$ M; $1\cdot10^{-6}$ M.

2.3. Procedure

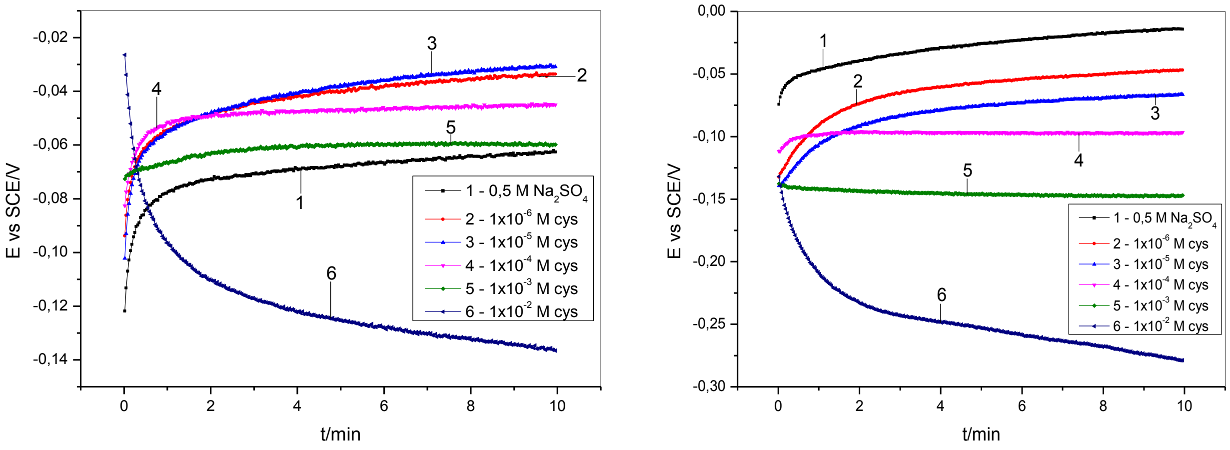
The apparatus used in electrochemical experiments consisted of a potentiostat, polarographic analyzer PA2 (Laboratorní Přístroje Praha, Czech Republic) which was directly connected to a computer via an AD card. The following methods were applied: the open circuit potential (OCP) measurements, potentiodynamic polarization in the form of linear voltammetry and chronoamperometry techniques. The open circuit potential was determined for 10 min upon which polarization curves were recorded from the open circuit potential to 0.5 V (SCE) in the anode direction and to -0.5 V (SCE) in the cathode direction. The measurements were performed at a scan rate of 1 mV s^{-1}. Chronoamperometric measurements were performed for 5 min at potentials of 0.0, 0.1 and 0.2 V

(SCE). All measurements were done at room temperature in naturally aerated solutions. The potential was expressed relative to the saturated calomel electrode (SCE). The pH values of the solutions were determined using pH metre CyberScan pH 510 Eutech. The electrode surface was examined by means of metalographic microscope Carl Zeiss Jena 413609 Epytip 2, and digital shots were taken.

3. RESULTS AND DISCUSSION

3.1. The open circuit potential measurements

From Fig. 3, containing mean values of 5 open circuit potential measurements, it can be seen that at lower cysteine concentrations in a neutral sodium sulphate solution, the potential value is more positive than in a blank sulphate solution. As the concentration increases, these values become more negative so that the open circuit potential value in the presence of $1 \cdot 10^{-2}$ M cysteine is more negative than the one recorded in a blank solution. As far as alkaline solutions are concerned, the trend clearly indicates that introducing cysteine into the system and increasing its concentration results in shifting the open circuit potential toward more negative values.



a) b)

Figure 3. Open circuit potential values of Cu electrode in a) neutral and b) alkaline sulphate solution with and without the addition of cysteine. Mean values of five measurements are presented.

Furthermore, the microscopic pictures of the electrode surface shown in Fig. 4 confirm the altered behaviour of copper in the presence of cysteine. A change in the colour of the electrode surface was observed indicating the formation of a film on the surface. This change is more pronounced with the increasing cysteine concentration.

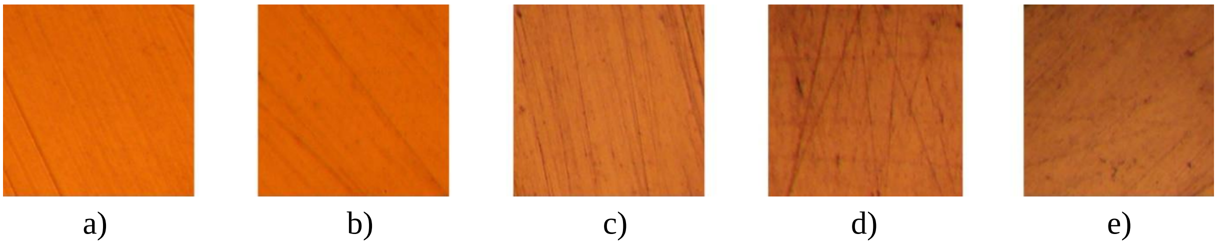


Figure 4. Electrode surface after a) polishing, measuring the open circuit potential during 10 min immersion in b) 0.5 M Na_2SO_4 pH 9 and with the addition of c) $1{\cdot}10^{-6}$ M, d) $1{\cdot}10^{-4}$ M and e) $1{\cdot}10^{-2}$ M cysteine (magnified 400x)

The shift in the open circuit potential can be ascribed to the adsorption of cysteine molecules [22, 23, 30, 31] or the formation of a complex containing copper and cysteine [28]. In the presence of lower cysteine concentrations in the solution, the potential values become more positive with time, whereas when the solution contains higher cysteine concentrations ($1{\cdot}10^{-2}$ M), the potential becomes more negative with time. The initial increase of the potential value points to the retardation of the cathode process, most probably caused by the inhibitory effect of the amino acid present in the medium and deposition ofcorrosion products. On the other hand, a negative shift of the potential value indicates retardation of the anode process due to the formation of an adsorbed layer [30]. It can be concluded that cysteine has an effect both on the anode and cathode process at the electrode surface acting like a mixed-type inhibitor. Furthermore, it was observed that the difference in the potential recorded with and without the inhibitor in a neutral sulphate solution did not exceed 85 mV, on the basis of which cysteine can be classified as a mixed-type inhibitor [32]. However, if the values of the open circuit potential obtained in alkaline solution are taken into consideration, it can be said that cysteine has a dominant effect on the cathode process under the said conditions.

3.2. Potentiodynamic polarization

The behavour of copper was studied during cathodic and anodic potentiodynamic polarization in sulphate solutions with and without the addition of cysteine. In the inhibitor free solution during anodic polarization copper undergoes dissolution [14, 33, 34] according to the following reactions:

$$Cu - e^- = Cu^+_{surf} \tag{1}$$

$$Cu^+_{surf} - e^- = Cu^{2+}_{sol} \tag{2}$$

wheras the cathodic reaction under these conditions is oxygen reduction which can be expressed as:

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{3}$$

However, the medium and its pH value have a significant effect on the behaviour and dissolution of copper. It can be observed in Fig. 5 and 6 (Curve1) showing potentiodynamic polarization curves recorded by using copper electrode in a 0.5 M sodium sulphate solutions of pH 7 and 9.

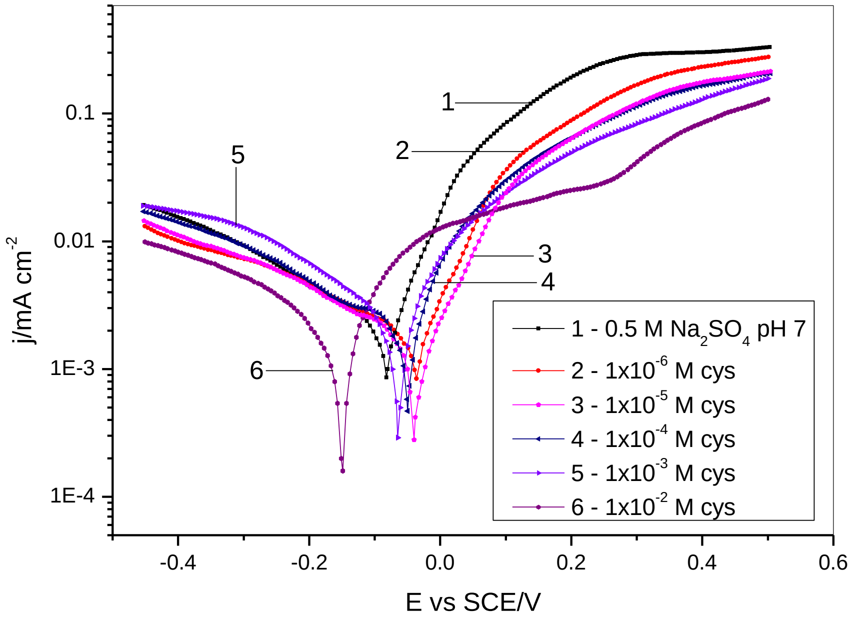


Figure 5. Potentiodynamic polarization curves recorded for copper in a neutral 0.5 M Na_2SO_4 solution with varying cysteine concentrations

It can be first observed that the curves are similar in shape, with higher current density recorded in a neutral solution. Anodic polarization of copper, both in a neutral and alkaline solution, leads to the formation of Cu(I) oxide. The formation of copper oxide at the electrode surface leads to passivation and prevents further corrosion of copper [35 - 40]. However, polarization graphs do not show decrease in current density with further increase in potential values. Rather, it shows a current plateau indicating that copper dissolution proceeds through the layer containing oxidation products [41]. This could be accounted for by the fact that, as sulphate ions tend to adsorb on copper surface [37, 38, 40, 42], competitive adsorption of hydroxyl and sulphate ions takes place on the surface. Furthermore, parallel reactions of copper with hydroxyl and sulphate ions occur whereby sulphate ions adsorbed on copper surface supress the reaction of copper oxide formation. That is why the anodic current density values are lower in alkaline than in neutral solutions since the former contain a higher concentration of hydroxyl ions exhibiting higher copper binding affinity [43]. The behaviour of copper during anodic polarization changes when cysteine is added to a sodium sulphate solution, which can be seen in Figures 5 and 6. What can be observed first is that the influence of cysteine depends on the pH value of the solution and its concentration in the solution. The inhibitory effect of cysteine is more expressed in the presence of lower concentrations in alkaline as compared to neutral solutions. It can be observed that copper oxidation process begins at more negative potentials as the cysteine concentration in the solution increases and that these values are more negative than in cysteine-free alkaline solutions. In neutral solutions, the presence of cysteine at a concentration lower than $1\cdot10^{-2}$ M influences copper behaviour, particularly in the vicinity of the corrosion potential due to adsorption at the electrode surface. As the potential increases the current density gravitates towards the value recorded in the cysteine-free solution. At a cysteine concentration of $1\cdot10^{-2}$ M, a current plateau occurs as a result of the Cu(I)-cysteine complex formation. Under these conditions the ongoing electrochemical process is controlled by the transfer of mass through the surface film. In the area of cathodic polarization, at a low cysteine concentration, a small peak occurs near the corrosion potential which can be accounted for by the reduction of copper oxidation products formed due to the immersion of the electrode in a sulphate solution during open circuit potential measurements [30, 33, 44]. At a $1\cdot10^{-3}$ M cysteine concentration, the current density recorded during cathodic polarization is higher than in a cysteine-free solution owing to the reduction of the Cu(I)-cys [45].

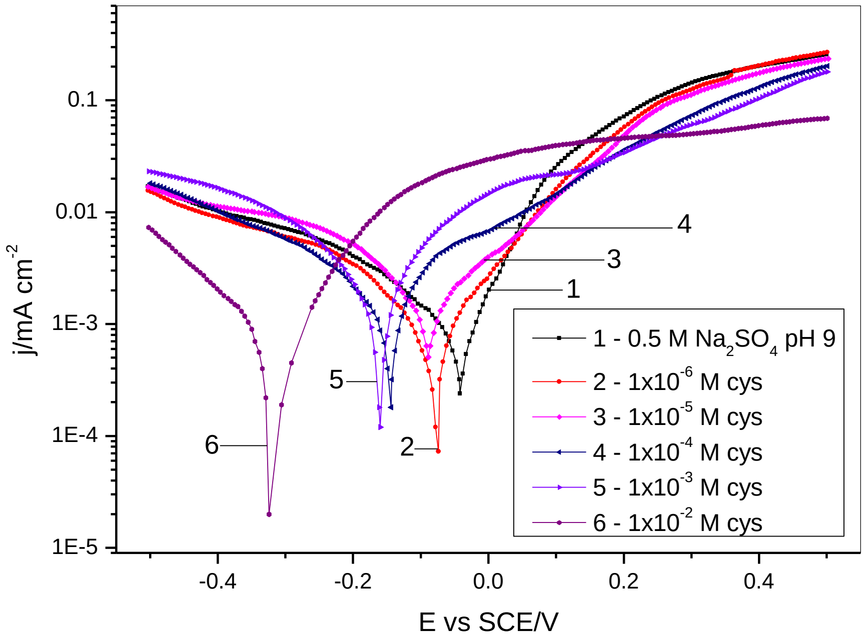


Figure 6. Potentiodynamic polarization curves recorded for copper in alkaline solution containing 0.5 M Na_2SO_4 with varying cysteine concentrations

In alkaline solutions, lower cysteine concentrations are sufficient to form a stable Cu(I)-cysteine complex, which can be noticedin potentiodynamic curves as a current plaeau encompassing a wider potential range with increasing cysteine concentration. A further increase in the potential value results in increased current density, with the curves approaching the one for a blank sodium sulphate solution. This can be interpreted in terms of the results obtained by Dursun and Nişli [45]. They found out that at pH 9.2 cysteine forms a complex with Cu(I) rather than with Cu(II), so that at higher potentials corresponding to Cu(II) formation, cysteine exhibits lower inhibition efficiency. Summing up the obtained results, a conclusion can be drawn that inhibitory effect of cysteine comes from the interaction with $Cu(I)_{ads}$, which is dominant at lower anodic potentials and that formation of the Cu(I)-cysteine film is the result of the following interaction:

$$Cu^{+} + cys = Cu(I)\text{-}cys \tag{4}$$

Owing to a high stability constant value [46, 47] this complex provides strong corrosion inhibition efficiency. At higher anodic potentials $Cu(II)_{ads}$ is formed having an unfavourable effect on adsorption. Such behaviour was reported by Matos et al. [28]. Cu(II) also influences oxidation of the Cu(I)-cys complex [44]. High inhibition efficiency during anodic polarization exhibited by amino acids containing a sulphur atom can be ascribed to their adsorption at anodic sites on the surface proceeding through the sulphur atom [19]. Consequently, the degree of surface coverage (θ) can be calculated as follows:

$$\theta = \frac{j_{corr} - j_{corr(inh)}}{j_{corr}} \tag{5}$$

The most suitable parameter for describing the effect of cysteine on copper dissolution during anodic polarization is inhibition efficiency (IE), whose value is calculated by using the following equation:

$$IE = \frac{j_{corr} - j_{corr(inh)}}{j_{corr}} \cdot 100\ [\%] \tag{6}$$

Where j_{corr} and $j_{corr(inh)}$ represent corrosion current density in the absence or presence of the inhibitor, respectively. The values obtained from the graphs shown in Fig. 5 and 6 are summed in Table 1. In general, an increased cysteine concentration enhances inhibition efficiency, which is somewhat higher in alkaline than in neutral solutions.

Table 1. Corrosion parameters obtained from polarization curves shown in Fig. 5 and 6

c_{cys}/ mol dm^{-3}	E_{corr}vs SCE/V	j_{corr}/µ A cm^{-2}	-b_c/V	b_a/V	IE (%)	E_{corr}vs SCE/V	j_{corr}/µ A cm^{-2}	-b_c/V	b_a/V	IE (%)
	pH 7					pH 9				
0	-0.080	3.700	0.522	0.120	0	-0.042	3.200	0.699	0.151	0
$1\cdot10^{-6}$	-0.036	2.000	0.472	0.094	45.95	-0.074	1.300	0.329	0.166	59.37
$1\cdot10^{-5}$	-0.040	1.800	0.396	0.122	51.35	-0.092	1.100	0.135	0.158	65.62
$1\cdot10^{-4}$	-0.050	1.300	0.120	0.070	64.86	-0.144	0.830	0.138	0.081	74.06
$1\cdot10^{-3}$	-0.065	1.100	0.089	0.065	70.27	-0.162	0.800	0.087	0.066	75.00
$1\cdot10^{-2}$	-0.149	0.900	0.120	0.080	75.68	-0.323	0.379	0.077	0.105	88.16

Upon careful examination of Fig. 7, it can be concluded that with increasing cysteine concentration, current density decreases exponentially while the degree of surface coverage increases exponentially. This points to the fact that the metal surface becomes saturated with the adsorbed cysteine molecules so that further increase in concentration does not lead to increased inhibition efficiency. Furthermore, some authors have reported reduced inhibition efficiency in the presence of high cysteine concentrations [22, 23].

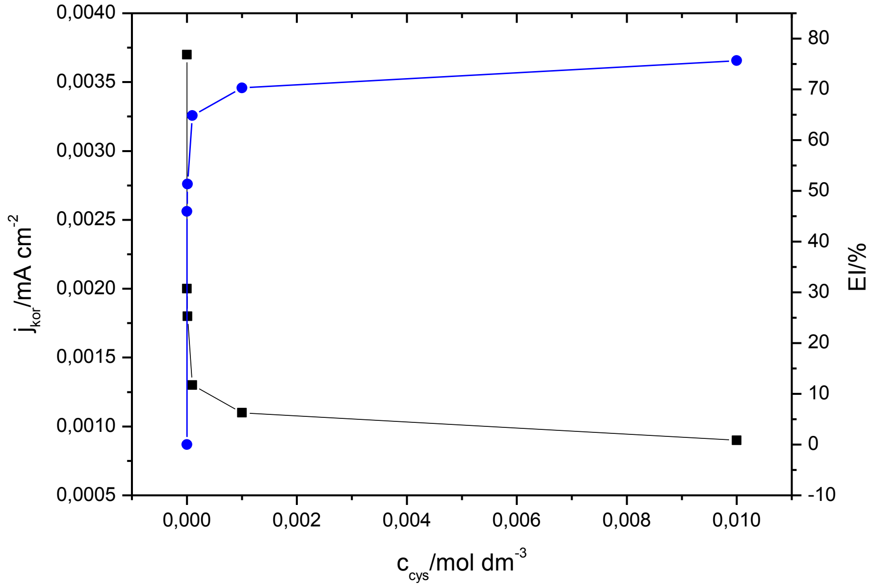


Figure 7. Dependence of corrosion current density (■) and inhibition efficiency (●) on cysteine concentration in a neutral 0.5 M sulphate solution

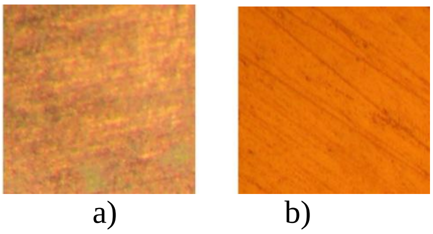

a) b)

Figure 8. The electrode surface after anodic polarization up to 0.5 V (SCE) in a) 0.5 M Na_2SO_4 pH 9 and b) in the presence of $1\cdot10^{-2}$ M cysteine (magnified 400x)

Fig. 8. shows microscopic photographs of the electrode surface after various treatments. During anodic polarization in sodium sulphate solution of pH 9, changes in the metal surface can be observed. Addition of cysteine to the solution has an effect on copper behaviour which is more pronounced as the cysteine concentration in the solution increases. At a cysteine concentration of $1\cdot10^{-2}$ M, there are no observable changes in the copper surface after anodic polarization.

3.3. Chronoamperometry

Chronoamperometry was used to examine the influence of constant potential applied to a copper electrode immersed in a 0.5 M sodium sulphate solution with and without cysteine. The experiments were carried out both in neutral and alkaline solutions. Chronoamperometric curves were recorded at potentials 0.0, 0.1 and 0.2 V (SCE). It was observed that with an increase in the potential to which the electrode was exposed, the current density also increased. It applies to the solutions with and without the inhibitor as well as to neutral and alkaline solutions. Chronoamperometric curves recorded at various potentials in alkaline sulphate solution containing $1\cdot10^{-6}$ M cysteine are shown in Fig. 9.

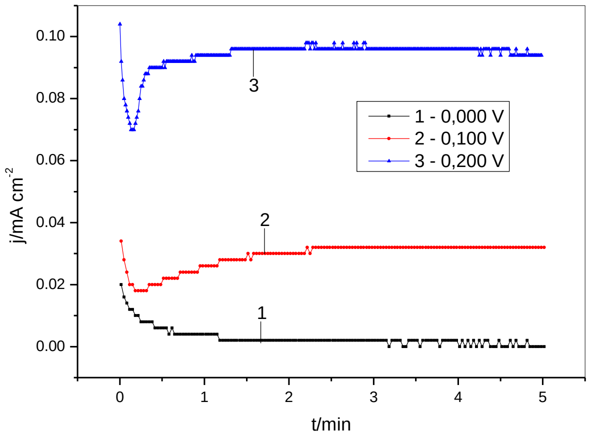


Figure 9. Chronoamperometric curves recorded in alkaline sulphate solution containing $1\cdot10^{-6}$ M cys at potentials 0.0, 0.1 and 0.2 V (SCE) for 5 min

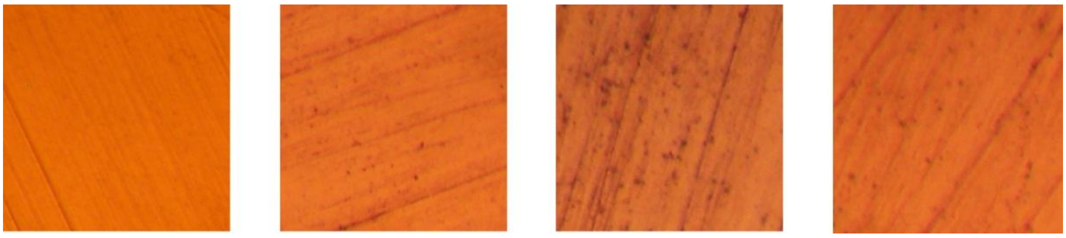
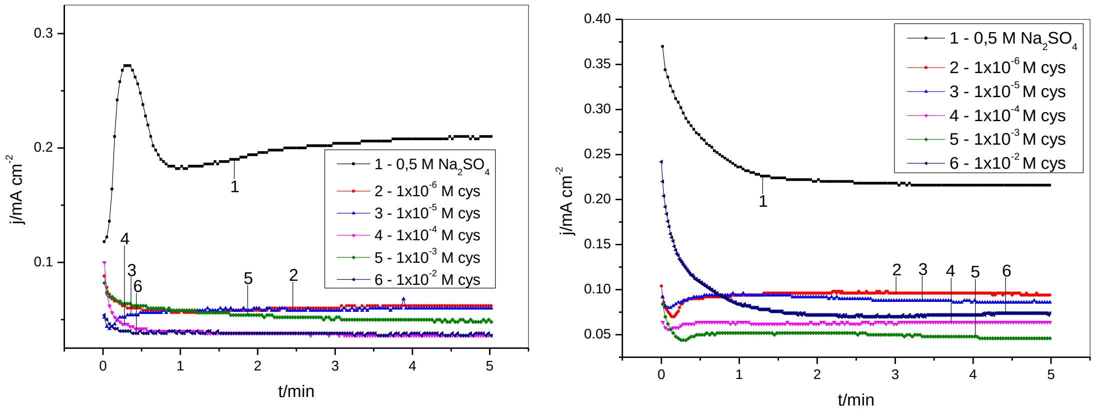

a) b) c) d)

Figure 10. The electrode surface after a) polishing, chronoamperometry for 5 min in a 0.5 M Na_2SO_4 solution pH 9 and with the addition of $1\cdot10^{-6}$ M cysteine at a potential b) 0.0 V (SCE), c) 0.1 V (SCE) and d) 0.2 V (SCE) (magnified 400x)

When chronoamperometric curves recorded in a $1\cdot10^{-6}$ M cysteine solution are compared with the micrographs of the electrode surface recorded after measuring (shown in Fig. 10) it can be observed that complementary results were obtained. More specifically, current density increases as the potential to which the electrode is exposed gets higher. Simultaneously, the micrographs show that several corrosion products are formed at the electrode surface. During polarization at a potential of 0.0

V (SCE), which is quite close to the opencircuit potential, it can be seen that initially the current has a somewhat higher value which rapidly decreases due to the formation of a protective film preventing further dissolution. The current reaches a constant value at which it reamains until the end of measurement. The low value of the current indicates that no pronounced corrosion process takes place at the applied potential. At potential values of 0.1 and 0.2 V (SCE) current density has a high initial value which then decreases as a result of a film formation. However, as can be observed, it subsequently increases indicating that dissolution takes place as the surface layer does not provide sufficient protection. The current quickly reaches a constant value and remains the same until the end of the measurement for 5 minutes. Similar behaviour was reported earlier [48].



a) b)

Figure 11. Chronoamperometric curves recorded in a) neutral sulphate solution containing various cysteine concentrations at a potential of 0.1 V (SCE) and b) alkaline sulphate solution containing various cysteine concentrations at a potential of 0.2 V (SCE)

The addition of cysteine reduces current density at all potentials and in all solutions. This effect becomes more pronounced as the concentration increases although there are some exceptions related to the highest cysteine concentration ($1\cdot10^{-2}$ M) in alkaline sulphate solutions. Nevertheless, as the calculated IE for these conditions is high, it cannot be ascribed to the activation effect but more likely, it is the result of a much more negative value of the corrosion potential than in other solutions. As an example, Fig. 11 shows chronoamperometric curves recorded in neutral and 0.5 M Na_2SO_4 alkaline solutions containing various cysteine concentrations at potentials of 0.1 and 0.2 V (SCE), respectively. The decreased current density in the presence of the inhibitor is generally attributed to adsorption of the inhibitor molecules [14, 49] and the formation of a protective layer at the electrode surface [50 - 52].

3.4. Adsorption mechanism

Cysteine is adsorbed on the copper surface and one of the models which potentially describes adsorption mechanism is the Langmuir adsorption isotherm. A number of studies [22 - 25] also indicate that cysteine adsorption proceeds according to the Langmuir isotherm, which is described by the following equation:

$$\frac{\theta}{1-\theta} = ACe^{\frac{-\Delta G}{RT}} = KC \qquad (7)$$

where K represents adsorption constant, ΔG is adsorption energy, C stands for cysteine concentration (mol dm^{-3}), whereas θ represents the degree of surface coverage. This equation can be also written as:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (8)$$

The relationship between the adsorption constant and adsorption energy is expressed as:

$$K = \frac{1}{55.55} e^{\frac{-\Delta G_{ads}}{RT}} \qquad (9)$$

which leads to $-\Delta G = \left(lnK - ln\frac{1}{55.55} \right) RT$ (10)

where R represents universal gas constant and T is thermodynamic temperature (293 K). By analysing the collected experimental data it can be seen that there is a linear dependence between cysteine concentration added to a 0.5 M Na_2SO_4 solution and the relationship between cysteine concentration and the degree of coverage (θ), both in neutral and alkaline solutions (Fig. 12). This means that each cysteine molecule replaces one water molecule on the copper surface. Furthermore, it is ideally considered that no interaction occurs between the molecules adsorbed on the metal surface. The slope of the Langmuir isotherm corresponding to the analysed data shows a small deviation from 1, which is characteristic for the ideal case. It is the result of the interaction between the adsorbed molecules [53, 54].

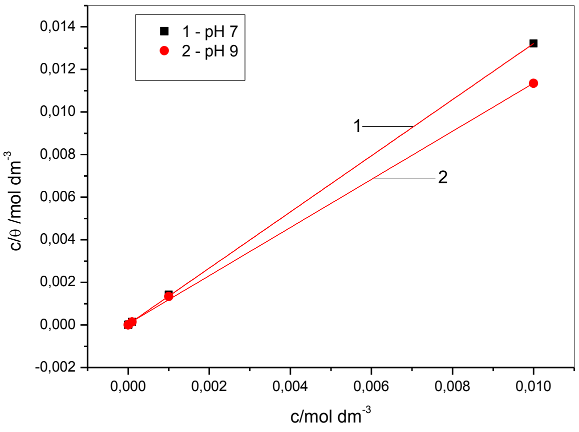


Figure 12. The Langmuir adsorption isotherm obtained from the data on copper behaviour in neutral and alkaline 0.5 M Na_2SO_4 solutions containing various cysteine concentrations

Based on the established adsorption model it is possible to calculate the Gibbs free energy of adsorption. From the results shown in Table 2, it can be seen that the values range from -30 to -40 kJ mol^{-1}, which points to a strong physical adsorption with slight chemisorption of cysteine on the copper surface under these conditions.

Table 2. Gibbs free energy of adsorption and R^2 for cysteine on copper in sodium sulphate solution

	Neutral solution	Alkaline soluion
ΔG/kJ mol^{-1}	-35	-34
R^2	0,99993	0,99961

Such behaviour can be expected considering the form and structure of cysteine in neutral and alkaline solutions. The sulphur-containing amino acids are characterized by their ability to be adsorbed as bidentate ligands with S atom as one and carboxyl or amino group the second adsorption centre. The availability of carboxyl or amino group depends on a solution pH. In neutral solutions, amino acid exists in the form of zwitter ions and can be attracted to anodic sites on the metal surface through a carboxyl group since a free electron pair of nitrogen atom is not available, thus blocking the sites that are active for corrosion. In the case of alkaline solutions, the amino acid occurs in the form of anions so that both amino and carboxyl group can take part in the adsorption process at the electrode surface [18].

4. CONCLUSION

The aim of this study was to investigate the effect of cysteine in the concentration range $1\cdot10^{-6}$ M - $1\cdot10^{-2}$ Mon electrochemical behaviour of copper in neutral (pH 7) and alkaline (pH 9) 0.5 M sodium sulphate solution. The methods used included determination of the open circuit potential, potentiodynamic and potentiostatic polarization. The addition of cysteine shifts the open circuit potential to a more negative region. Cysteine influences copper electrode behaviour during anodic potentiodynamic polarization in the vicinity of the corrosion potential, whereas at higher potential values copper behaves similarly as in a cysteine-free solution. This can be attributed to inhibitory action through $Cu(I)_{ads}$, which is a dominant species in the region of lower anodic potentials, as well as the formation of the Cu(I)-cys film on the metal surface. At higher anodic potentials $Cu(II)_{ads}$ occurs, which is unfavourable for the adsorption of cysteine. Generally, inhibition efficiency increases with the increasing cysteine concentration. Chronoamperometric results indicate that as the electrode potential increases, the current density increases as well. The addition of cysteine results in decreased current density at all potentals and in all solutions. The adsorption of cysteine on copper surface in neutral and alkaline sodium sulphate solutions proceeds in accordance with the Langmuir adsorption isotherm.

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References

1. M.M. Antonijević, S.C. Alagić, M.B. Petrović, M.B. Radovanović and A.T. Stamenković, *Int. J. Electrochem. Sci.*, 4 (2009) 516
2. M.M. Antonijević, G.D. Bogdanović, M.B. Radovanović, M.B. Petrović and A.T. Stamenković, *Int. J. Electrochem. Sci.*, 4 (2009) 654
3. Y. Feng, K.-S. Siow, W.-K. Teo, K.-L. Tan and A.-K. Hsieh, *Corrosion*, 53 (1997) 389
4. M. Edwards, J. Rehring and T. Meyer,*Corrosion*, 50 (1994) 366
5. M.M. Antonijević and M.B. Petrović, *Int. J. Electrochem. Sci.*, 3 (2008) 1
6. M.M. Antonijević, S.M. Milić and M.B. Petrović, *Corros. Sci*,. 51 (2009) 1228
7. M.M. Antonijević, S.M. Milić, S.M. Šerbula and G.D. Bogdanović, *Electrochim. Acta*, 50 (2005) 3693
8. S.M. Milić, M.M. Antonijević, S.M. Šerbula and G.D. Bogdanović, *Corros. Eng. Sci. Techn.*, 43 (2008) 30
9. S.M. Milić and M.M. Antonijević, *Corros. Sci.*, 51 (2009) 28
10. M.M. Antonijević, S.M. Milić, M.B. Radovanović, M.B. Petrović and A.T. Stamenković, *Int. J. Electrochem. Sci.*, 4 (2009) 1719
11. M.M. Antonijević, S.M. Milić, M.D. Dimitrijević, M.B. Petrović, M.B. Radovanović and A.T. Stamenković, *Int. J. Electrochem. Sci.*, 4 (2009) 962
12. W. Qafsaoui, Ch. Blanc, J. Roques, N. Pébère, A. Srhiri, C. Mijoule and G. Mankowski, *J. Appl. Electrochem.*, 31 (2001) 223
13. M.M. El-Naggar, *J. Mater. Sci.*, 35 (2000) 6189
14. M. Scendo, *Corros. Sci.*, 49 (2007) 2985
15. M. Scendo, *Corros. Sci.*, 49 (2007) 3953
16. M.B. Petrović, A.T. Simonović, M.B. Radovanović, S.M. Milić and M.M. Antonijević, *Chem. Pap.*, 66 (2012) 664
17. Z. Ghasemi and A. Tizpar, *Appl. Surf. Sci.*, 252 (2006) 3667
18. M.M. El-Rabiee, N.H. Helal, Gh.M. Abd El-Hafez and W.A. Badawy, *J. Alloy. Compd.*, 459 (2008) 466
19. M.S. Morad, *J. Appl. Electrochem.*, 38 (2008) 1509
20. K. Barouni, L. Bazzi, R. Salghi, M. Mihit, B. Hammouti, A. Albourine and S. El Issami, *Mater. Lett.*, 62 (2008) 3325
21. D.-Q. Zhang, L.-X. Gao and G.-D. Zhou, *J. Appl. Electrochem.*, 35 (2005) 1081
22. W.A. Badawy, K.M. Ismail and A.M. Fathi, *Electrochim. Acta*, 51 (2006) 4182
23. K.M. Ismail, *Electrochim. Acta*, 52 (2007) 7811
24. M. A. Kiani, M.F. Mousavi, S. Ghasemi, M. Shamsipur and S.H. Kazemi, *Corros. Sci.*, 50 (2008) 1035
25. M.S. Morad, *J. Appl. Electrochem.*, 35 (2005) 889
26. G. Bereket and A. Yurt, *Corros. Sci.*, 43 (2001) 1179
27. A.B. Silva, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro and E. D’Elia, *Corros. Sci.*, 48 (2006) 3668
28. J.B. Matos, L.P. Pereira, S.M.L. Agostinho, O.E. Barcia, G.G.O. Cordeiro and E. D' Elia, *J. Electroanal. Chem.*, 570 (2004) 91
29. M.B. Radovanović, M.B. Petrović, A.T. Simonović, S.M. Milić and M.M. Antonijević, *Environ. Sci. Pollut. Res.*, in press (2012) DOI 10.1007/s11356-012-1088-5

30. H. Saifi, M.C. Bernard, S. Joiret, K. Rahmouni, H. Takenouti and B. Talhi, *Mater. Chem. Phys.*, 120 (2010) 661
31. E.E. Oguzie, Y. Li and F.H. Wang, *Electrochim. Acta*, 53 (2007) 909
32. E.S. Ferreira, C. Giacomelli, F.C. Giacomelli and A. Spinelli, *Mater. Chem. Phys.*, 83 (2004) 129
33. G. Moretti and F. Guidi, *Corros. Sci.*, 44 (2002) 1995
34. E. Hamed, *Mater. Chem. Phys.*, 121 (2010) 70
35. G. Bertrand, E. Rocca, C. Savall, C. Rapin, J.-C. Labrune and P. Steinmetz, *J. Electroanal. Chem.*, 489 (2000) 38
36. N. Huynh, S.E. Bottle, T. Notoya and D.P. Schweinsberg, *Corros. Sci.*, 44 (2002) 2583
37. R.M. Souto, S. González, R.C. Salvarezza and A.J. Arvia, *Electrochim. Acta*, 39 (1994) 2619
38. K.M. Ismail, A.M. Fathi and W.A. Badawy, *J. Appl. Electrochem.*, 34 (2004) 823
39. G. Mankowski, J. P. Duthil and A. Giusti, *Corros. Sci.*, 39 (1997) 27
40. D. Tromans and R.-H. Sun, *J. Electrochem. Soc.*, 139 (1992) 1945
41. E. Sidot, N. Souissi, L. Bousselmi, E. Triki and L. Robbiola, *Corros. Sci.*, 48 (2006) 2241
42. K.M. Ismail, R.M. Elsherif and W.A. Badawy, *Electrochim. Acta*, 49 (2004) 5151
43. V. Maurice, L.H. Klein, H.-H. Strehblow and P. Marcus,*J. Electrochem. Soc.*, 150 (2003) B316
44. G.Quartarone, T.Bellomi and A.Zingales, *Corros. Sci.*, 45 (2003) 715
45. Z. Dursun and G. Nişli, *Talanta*, 63 (2004) 873
46. A. Rigo, A. Corazza, M.L. di Paolo, M. Rosserro, R. Ugolini and M. Scarpa, *J. Inorg. Biochem.*, 98 (2004) 1495
47. M.S. El-Deab, *Mater. Chem. Phys.*, 129 (2011) 223
48. I. Mabille, A. Bertrand, E.M.M. Sutter and C. Fiaud, *Corros. Sci.*, 45 (2003) 855
49. E.-S.M. Sherif, R.M. Erasmus and J.D. Comins, *Corros. Sci.*, 50 (2008) 3439
50. B. Assouli, Z.A. Ait Chikh and A. Srhiri, *Polymer*, 42 (2001) 2449
51. M. Elbakri, R. Touir, M. Ebn Touhami, A. Srhiri and M. Benmessaoud, *Corros. Sci.*, 50 (2008) 1538
52. F.X. Perrin, M. Wery and J. Pagetti, *J. Appl. Electrochem.*, 27 (1997) 821
53. M. Scendo, *Corros. Sci.*, 49 (2007) 373
54. F. Touhami, A. Aouniti, Y. Abed, B. Hammouti, S. Kertit, A. Ramdani and K. Elkacemi, *Corros. Sci.*, 42 (2000) 929