

## Corrosion Inhibition of Copper Metal by Some Amino Acids in Chloroacetic Acids

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**Abstract:** The corrosion behavior of copper metal in chloroacetic acids, namely monochloroacetic acid (MCA), dichloroacetic acid (DCA) and tri chloroacetic acid (TCA), were investigated using potentiodynamic and cyclic voltammetry techniques. It was found that, for diluted solutions of DCA and TCA (< 0.5M) and all MCA concentrations only active and limiting current regions were appeared but on increasing the concentration of DCA and TCA to above  $\geq 0.5M$  a new region appears directly before limiting current region characterized by oscillation in current density. Scanning electron microscopy (SEM) and EDX pattern refer to that the porosity of electrode surface is in lose relation with appearances of current oscillation phenomena. The inhibition effect of alanine, valine and phenylalanine was examined. Calculated quantum chemical parameters indicated that the trend for variation of corrosion inhibition of studied amino acids is consists with the trend deduced from experimental results. Different adsorption isotherms were tested.

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**Keywords:** Copper; Corrosion; inhibition; polarization; amino acids

### 1. Introduction

Copper is known for plenty of favorable physical, chemical and mechanical properties which resulting in widely exploitation of copper in different types of industry. Due to its broad application, corrosion of copper is considered as a significant issue. Therefore, investigation of corrosion and corrosion inhibition of copper are widely studied [1-5].

Inhibition of corrosion can be effectively applied only if mechanism that leads to corrosion is thoroughly understood. Electrochemical nature of corrosion – passivation phenomenon can consequently lead to appearance of current oscillations. Such oscillations contain information on corrosion – passivation process at the surface of electrode. Current oscillations during the copper electrodisolution have been widely investigated in inorganic acidic aqueous electrolytes [6-10]. On contrary, only a few experimental achievements have been reported on the sustained current oscillations during the copper electrodisolution in organic acidic aqueous or non aqueous electrolytes [11-13].

The use of inhibitors seems to be the best way to overcome the copper electrodisolution problem. The conventional organic and inorganic corrosion inhibitors are environmentally hazardous; therefore, it is important to select environmentally safe materials that can be used as corrosion inhibitors such as amino acids compounds [14].

The goal of this study is to gain better insight the electrodisolution of copper in monochloroacetic (MCA), dichloroacetic (DCA) and trichloroacetic (TCA) acids solutions and evaluate some amino acids as corrosion inhibitors in these media.

### 2. Experimental:

The material used in the present study was spectroscopically pure copper rod electrode (99.999%). A specimen holder was used to expose 1cm<sup>2</sup> surface area. The area shielded by the specimen holder was then coated with a protective enamel to prevent crevice corrosion. The exposed surface specimen was prepared by polishing with a sequence of sand paper (600,800 and 1200) grids, cleaning several times with deionized water and drying with acetone before immersing in the test solution. The cell was equipped with Pt counter electrode and saturated calomel electrode (SCE) reference electrode. Curves were recorded potentiodynamically, by using Volta Lab PGZ301 Dynamic EIS Voltammetry, under aerated conditions beginning by one hour hold in test solution at open circuit. Deionized water used to prepare solutions at room temperature (30±2°C). The percentage inhibition efficiency (%IE) and degree of surface coverage ( $\theta$ ) of the investigated surfactant compounds were calculated from the following equations:

$$\%IE = [1 - (i_{\text{corr (inh)}} / i_{\text{corr (free)}})] \times 100 \quad (1)$$

$$\theta = [1 - (i_{\text{corr (inh)}} / i_{\text{corr (free)}})] \quad (2)$$

Where  $i_{\text{corr (free)}}$  and  $i_{\text{corr (inh)}}$  are the corrosion current densities in absence and presence of inhibitors.

All the quantum chemical calculations were performed with MOPAC 2008 semi-empirical program using MNDO method.

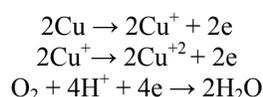
### 3. Result and Discussion:

Fig.1 represents the current density – potential (I - E) polarization curves for the copper electrode in

aerated solutions of MCA, DCA and TCA at various concentrations ranging from 0.05M to 1.0M. The curves swept from -150mV (SCE) to 1600mV (SCE) at scan rate of 10mV/s.

As shown in Fig.1, for all polarization curves, two main potential regions can be distinguished. In region I active electrodisolution of copper takes place, this region is often named the active region. The active region could be further divided into two sub - regions: the Tafel region, located at lower potentials, where  $I$  exponential increases with  $E$ , according the Tafel behavior ( $\log i - E$ ); a sub – region that follows the Tafel region, located at higher potential, where  $I$  increases linearly with  $E$ .

In fact, corrosion of copper in aerated acid solutions is a result of two partial reactions [15]: The successive anodic reactions, which can be written as:



Therefore, it is probable that, the immersion of copper electrode in such acids is accompanied first by dissolution of the metal to yield  $\text{Cu}^+$  ion in solution. During the electrodisolution process a large quantity of copper ions are present in the electrode / electrolyte interface and in order to preserve the electroneutrality, chloroacetate anions migrate towards the electrode surface and  $\text{H}^+$  ions migrate towards bulk solution. As a result, the formation of the film on the surface of the copper electrode was encouraged by the precipitation of the saturated concentration of copper and chloroacetate anions in the electrode / electrolyte interface. When the formation and dissolution of such film on the surface of electrode proceed at equal rates, the mass – transfer limiting current plateau or the limiting current region, region II, is appeared.

Moreover, since the corrosion of copper depends on several factors, among which are the complex ion formation, the solubility of reaction products, the concentration of  $\text{Cl}^-$  ions and oxygen content of solution [16], it is suggested that the probable formation of insoluble basic chlorides in addition to chloroacetate compounds would be occur.

As observed in Fig. 1, for diluted solutions of DCA and TCA ( $< 0.5\text{M}$ ) and in all MCA concentrations the two above regions are only present but on increasing the concentration of DCA and TCA to above  $\geq 0.5\text{M}$  a new region appears directly before limiting current region characterized by oscillation in current density.

The corrosion parameters of copper electrode in MCA, DCA and TCA solutions are given in Table. 1. It is clear that, the corrosion current density,  $I_{\text{corr}}$ , and the corrosion rate,  $\text{CR}$ ., increase by increasing in acids concentrations in order of  $\text{TCA} > \text{DCA} > \text{MCA}$ .

This may be attributable to that the relative ease of hydrolysis of TCA, which produces  $\text{HCl}$ , whereas the hydrolysis of DCA is more difficult and hydrolysis of MCA is much more difficult [17].

As clear from results, for Cu/DCA and Cu/TCA systems, corrosion process occurs before appearances of current oscillations which mean that a corrosion reaction was done on the electrode surface. In order to study the origin of current oscillation phenomena a cyclic voltametric were carried out.

Fig.2 represent a cyclic voltametric (CV.) measurements for copper electrode in 0.5M of MCA, DCA and TCA using a scan rate of 10mV/s in potential range similar to potentiodynamic polarization one. However, when the forward anodic potential reaches the value of 1600mV<sub>(SCE)</sub> it reversed in the backward anodic potential with the same scan rate.

The curve obtained for Cu/MCA system, Fig.2, show that the backward (negative) scan identical with forward (positive) curves one, indicating that the solution under these conditions does not cause any pitting corrosion. However, for (I-E) curves of Cu/DCA and Cu/TCA systems, the backward scan form a large hysteresis loop indicating the electrode susceptible to pitting corrosion, also, oscillation in current were observed in both forward and backward potential scans.

In Cu/TCA system, in the forward potential scan, the anodic dissolution current increases almost linearly as the potential swept from 0 to about 0.49V<sub>(SCE)</sub>, then current oscillation are observed until the potential reaches about 1.26V<sub>(SCE)</sub> when the current decreases to low value. The polarization behavior in backward sweep resembles that in the forward one. The same I-E pattern was observed in Cu/DCA with increasing in the amplitudes of the current oscillations.

EDX patterns of copper electrode after it was electrochemically treated with 0.5M DCA, Fig.3a, and 0.5M TCA, 3b, by using CV. Conditions indicate that the surface film of the electrode is rich in chloride. In order to study this quantitative description of the origin of current oscillatory phenomena a scanning electron microscope (SEM) was applied. As it is clear from SEM for copper electrode, Fig.4, the microstructure for specimens surface immersed in 0.5M DCA, Fig.4b, and 0.5M TCA, Fig.4c, showed heterogeneous surface morphology characterized by groves with extensive pits over the entire alloy surface, indicating that pitting corrosion is the mode of degradation, while in 0.5M MCA, Fig.4a, copper specimens surface corroded uniformly indicating that the uniform corrosion is the reason for degradation.

Based on these observations it may be concluded that the porosity of electrode surface is in close relation with appearances of current oscillation of copper electrode in both DCA and TCA media and the

observed porous film was assigned to insoluble CuCl salt in agreement with previous authors [6-10,18].

Since 0.5M was the concentration of beginning appearances of current oscillatory phenomena of copper electrode in both of DCA and TCA solutions, so it was chosen to study the efficiency of valine, alanine and phenyl alanine in retardation of pitting corrosion in Cu/DCA and Cu/TCA systems.

Inspection of electrochemical parameters values given in Table 2 reveals that, by increasing the concentration of the three respective amino acids the corrosion current density,  $I_{corr.}$ , decreases by notable increase in inhibition efficiency, %IE, which means the dependants of %IE on the concentration of the used amino acids. Table 2 also reveals that, the trend for the variation of inhibition efficiency is:

Phenyl alanine > valine > alanine

As is clear from Fig.5, which represents CV curves for copper electrode in 0.5M DCA and TCA solutions containing 0.2M of the used amino acids, the addition of the respective amino acids calm down the overall current oscillatory behavior of the electrochemical system. Comparative analysis of oscillation region,  $E_{osci.}$ , in solution with and without additives suggest that, in solution containing 0.2M additive, the bifurcation point appear at low anodic potential causing shrinking of  $E_{osci.}$ , which means that the given system achieved minimum oscillatory response with smallest  $E_{osci.}$  and stable steady state. Furthermore, current oscillatory phenomena completely disappear in the forward and backward scans of Cu/DCA system containing 0.2M phenyl alanine. In general, the hysteresis loop observed during the reverse scan is diminished indicating improving in the surface condition which was confirmed by SEM, Fig.6.

The inhibition process is based on the adsorption of the amino acid molecules on the active sites and/or desorption of the corrosion products on the metal surface [19]. This process depends on both the nature of the amino acid and the state of the metal surface. In acidic solution, the amino acid molecule is present in protonated form [20]. However, it is well known that the presence of aromatic ring, hetero atoms, or long chain aliphatic groups on the amino acid structure causes significant increase in inhibition efficiency. So, the better efficiency of valine compared with alanine related to the more methylene's in its molecular structure. The electron donating effect of methyl group in valine cause electron density on the  $-NH_2$  will be higher than electron density on  $-NH_2$  group of alanine. Electrons in aromatic ring of phenyl alanine can be shared to copper orbital forming insoluble complex that protected the surface from aggressive  $Cl^-$  ions [21].

### Adsorption Isotherm:

In order to get more information about the mode of adsorption of the respective amino acids on the copper electrode surface, the data obtained from CV techniques have been tested with several adsorption isotherms including Langmuir, Temkin, Freundlich, Frumkin and kinetic thermodynamic adsorption models. The testes indicated that the adsorption of the studied amino acids on copper surface is best described by Langmuir, Temkin and adsorption model.

Langmuir adsorption isotherm relationship is represented by equation [22]:

$$\log (C/\theta) = \log C - \log k \quad (3)$$

where C is the concentration of the inhibitor in the bulk electrolyte,  $\theta$ , is the surface coverage by inhibitor molecules and K is the equilibrium constant of adsorption. Plots of  $\log (C/\theta)$  vs.  $\log C$  are shown in Fig.7. Values of adsorption parameters deduced from the isotherms are presented in Table 3. From the results obtained, the  $R^2$  values for the plots are closer to unity, indicating that the adsorption of the studied amino acids is consistent with the Langmuir adsorption model.

Temkin adsorption isotherm is given by the general equation [23].

$$\ln KC = a\theta \quad (4)$$

where (a) is a parameter characterizing the interaction between the adsorbed particles, the homogeneity of the surface and measuring the steepness of the adsorption isotherm. Plots of  $\theta$  vs.  $\log C$  are shown in Fig. 7. The data gave straight line including with  $R^2$  values that The Temkin's adsorption isotherm is valid for these amino acids.

On the other hand, it is found that the kinetic thermodynamic model [23]

$$\log (\theta/1-\theta) = \log K^{\lambda} + y \log C \quad (5)$$

is valid to operate the present adsorption data. The equilibrium constant of adsorption ( $K = K^{\lambda} (1/y)$ ), where  $1/y$  is the number of the surface active sites occupied by one inhibitor molecules. Plotting  $\log (\theta/1-\theta)$  vs.  $\log C$  given in Fig. 7 where straight line relationships were obtained suggesting with  $R^2$  values validity of this model for the studied case. The positive values of (a), Table 3, imply that the interaction between molecules which causes an increase in the adsorption energy with increases in  $\theta$  values.

The equilibrium constant of adsorption deduced from the Langmuir, Temkin and kinetic thermodynamic adsorption models is related to free energy of adsorption of the inhibitor as follows [22]:

$$\Delta G_{\text{ads}}^{\circ} = -2.303RT * \log(55.5K) \quad (6)$$

Where 55.5 is the molar concentration of water,  $\Delta G_{\text{ads}}^{\circ}$ , is the free energy of adsorption of the inhibitor, R, is the gas constant and T, is the temperature. Calculated values of the free energy are recorded in Table 3. From the results obtained, the free energies are negative in values expected for the mechanism of chemical adsorption. Therefore, the adsorption of the studied amino acids on the copper surface is spontaneous and is consistent with the mechanism of electrostatic transfer of charge from the charged inhibitor's molecules to charged metal surface which supports physisorption.

### Theoretical Study:

The effectiveness of inhibitor can be related to its spatial molecular structure as well as with their molecular electronic structure [24]. Also there are certain quantum chemical parameters that can be related to the interactions metal inhibitor. Among these, we can mention the  $E_{\text{HOMO}}$ , energy of the highest occupied molecular orbital, that is often associated with the capacity of a molecular donate electrons. Therefore, increase in the values of  $E_{\text{HOMO}}$ , can facilitate the adsorption and therefore the inhibition efficiency, by indicating the disposition of the molecule to donate orbital electrons to an appropriate acceptor with empty molecular orbital. On the other hand,  $E_{\text{LUMO}}$ , energy of the lowest unoccupied

molecular orbital, indicates the ability of the inhibitor's molecule to accept electrons, which implies that the inhibition efficiencies of the studied amino acids are expected to increase with decreasing  $E_{\text{LUMO}}$  values [25, 26]. From the results obtained for  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , Table 4, can be stated that the inhibition efficiency of the studied amino acids are consistent with the trend obtained from experimental results.

If it is assumed that after physical adsorption, chemisorption of organic molecules occurs due to chelation on metal surface by donation of electrons to unoccupied d-orbital, using anti-bonding molecular orbital, then the formation of a feedback bond would be characterized by increasing values of  $E_{\text{HOMO}}$  and decreasing values of  $E_{\text{LUMO}}$ , which is proposed for the observed trend. The energy gap ( $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$ ) of inhibitors is another parameter that can be used to predict the extent of corrosion inhibition. Large values of the energy gap imply low reactivity to a chemical species. From the results of the study, the inhibition efficiency of the studied amino acids was found to be increase with the decreasing values of the energy gap and the trend is consistent with experimental results [27]. Table 3, also presents the calculated values of the dipolmoment,  $\mu$ . Similarly, low values of  $\mu$  will favor the accumulation of the inhibitor molecules on the metallic surface [27], the expected trend for the variation of inhibition efficiency is also consistent with the trend deduced from frontier molecular energies [28].

**Table (1): Electrochemical parameters of copper electrode in different concentrations of MCA, DCA and TCA solutions at 30°C.**

	Conc. (M)	$E_{\text{corr.}}$ (V)	$I_{\text{corr.}} \times 10^{-3}$ (mA/cm <sup>2</sup> )	Rp (ohm.cm <sup>2</sup> )	Tafel slopes		Corrosion rate mm/y
					$B_a$ (mv)	$B_c$ (mv)	
MCA	0.05	-15.000	0.033.4258	-852.180	94.100	-156.300	0.391
	0.1	-15.200	0.052	240.130	78.300	-144.800	0.608
	0.5	-18.100	0.070	313.910	68.900	-142.800	0.813
	0.7	-8.700	0.093	429.160	85.600	-184.600	1.085
	1	12.200	0.097	-140.440	89.400	-156.700	1.139
DCA	0.05	-20.300	0.078	363.570	79.200	-146.000	0.906
	0.1	-21.600	0.085	-67.730	66.000	-135.400	0.995
	0.5	-23.100	0.105	52.690	61.800	-124.200	1.230
	0.7	-6.800	0.105	40.690	73.500	-143.300	1.230
	1	-10.400	0.111	15.190	63.000	-140.800	1.301
TCA	0.05	-12.800	0.086	76.450	62.000	-135.600	1.003
	0.1	-22.100	0.099	19.050	59.500	-131.400	1.161
	0.5	-28.600	0.114	219.710	48.900	-107.900	1.336
	0.7	-31.700	0.141	-14.750	51.000	-113.100	1.645
	1	-31.000	0.177	-5.370	51.800	-114.700	2.067

Table (2): Electrochemical parameters of copper electrode in 0.5M DCA and 0.5TCA solutions containing different concentrations of alanine, valine and phenyl alanine at 30°C

	Conc. (M)	E <sub>corr.</sub> (V)	I <sub>corr.</sub> × 10 <sup>-3</sup> (mA/cm <sup>2</sup> )	Tafel slopes		%IE
				B <sub>a</sub> (mv)	B <sub>c</sub> (mv)	
DCA	0.5	-23.1	0.1052	61.8	-124.2	--
	<b>Alanine</b>					
	+0.01	-48.9	0.0768	104.0	-82.5	26.9962
	+0.05	-42.2	0.0631	80.1	-86.1	40.01901
	+0.1	-40.0	0.0419	90.2	-76.1	60.1711
	+0.2	-33.1	0.0432	76.2	-97.8	58.93536
	<b>Valine</b>					
	+0.01	-31.6	0.0741	115.2	-107.9	29.56274
	+0.05	-32.2	0.0402	100.7	-102.9	61.78707
	+0.1	-27.8	0.0417	88.6	-103.7	60.36122
	+0.2	-30.3	0.0394	90.8	-100.8	62.54753
	<b>Phenyl alanine</b>					
	+0.01	-16.2	0.0520	63.8	-109.6	50.57034
	+0.05	-22.8	0.0492	56.3	-92.1	53.23194
	+0.1	-16.7	0.0383	68.7	-104.9	63.59316
	+0.2	-23.1	0.0372	55.4	-99.2	64.63878
TCA	0.5	-28.6	0.1142	48.9	-107.9	--
	<b>Alanine</b>					
	+0.01	-64.9	0.1078	131.0	-75.9	5.604203
	+0.05	-66.3	0.0946	128.0	-73.3	17.16287
	+0.1	-60.9	0.0720	107.6	-76.1	36.95271
	+0.2	-45.6	0.06187	89.5	-83.1	45.82312
	<b>Valine</b>					
	+0.01	-28.9	0.1022	62.7	107.5	10.50788
	+0.05	-32.2	0.0905	67.6	-90.7	20.75306
	+0.1	-29.4	0.0794	58.8	-107.5	30.47285
	+0.2	-24.3	0.0467	62.6	-108.4	59.10683
	<b>Phenyl alanine</b>					
	+0.01	-33.0	0.0602	60.9	-112.3	47.28546
	+0.05	-36.3	0.0540	56.3	-109.9	52.71454
	+0.1	-34.1	0.0479	57.6	-102.3	58.05604
	+0.2	-34.0	0.0401	69.7	-88.5	64.88616

Table (3): Adsorption parameters for the studied amino acids on copper surface.

DCA	alanine	valine	phenyl alanine	TAC	alanine	valine	phenyl alanine
<b>Langmuir</b>							
R <sup>2</sup>	0.988	0.973	0.998		0.872	0.941	0.999
ΔG <sup>0</sup> <sub>ads</sub> kJmol <sup>-1</sup>	-5.174	-5.813	-7.834		1.369	-1.028	-7.587
LogK	-0.852	-0.742	-0.394		-1.980	-1.567	-0.437
<b>Temkin</b>							
R <sup>2</sup>	0.895	0.818	0.828		0.923	0.799	0.929
ΔG <sup>0</sup> <sub>ads</sub> kJmol <sup>-1</sup>	-10.171	-9.654	-7.939		-11.795	-10.120	-10.120
LogK	0.009	-0.080	-0.376		0.289	0.285	-0.330
a	0.624	0.599	0.269		0.727	0.773	0.300
<b>Kinetic model</b>							
R <sup>2</sup>	0.905	0.818	0.826		0.980	0.903	0.923
ΔG <sup>0</sup> <sub>ads</sub> kJmol <sup>-1</sup>	-21.758	-12.204	-26.719		-10.163	-10.120	-10.120
LogK	0.250	0.359	2.861		0.250	0.359	2.861
1/y	2.006	2.114	4.785		0.007	0.021	2.155

**Table (4): Quantum chemical parameters for the studied amino acids**

Quantum parameters	EHOMO (ev.)	ELUMO (ev.)	$\Delta E$ (ev.)	$\mu$ (Debye)
alanine	-9.70	0.97	10.67	1.89
valine	-9.67	.096	10.63	2.29
Phenyl alanine	-9.63	0.33	9.96	2.04

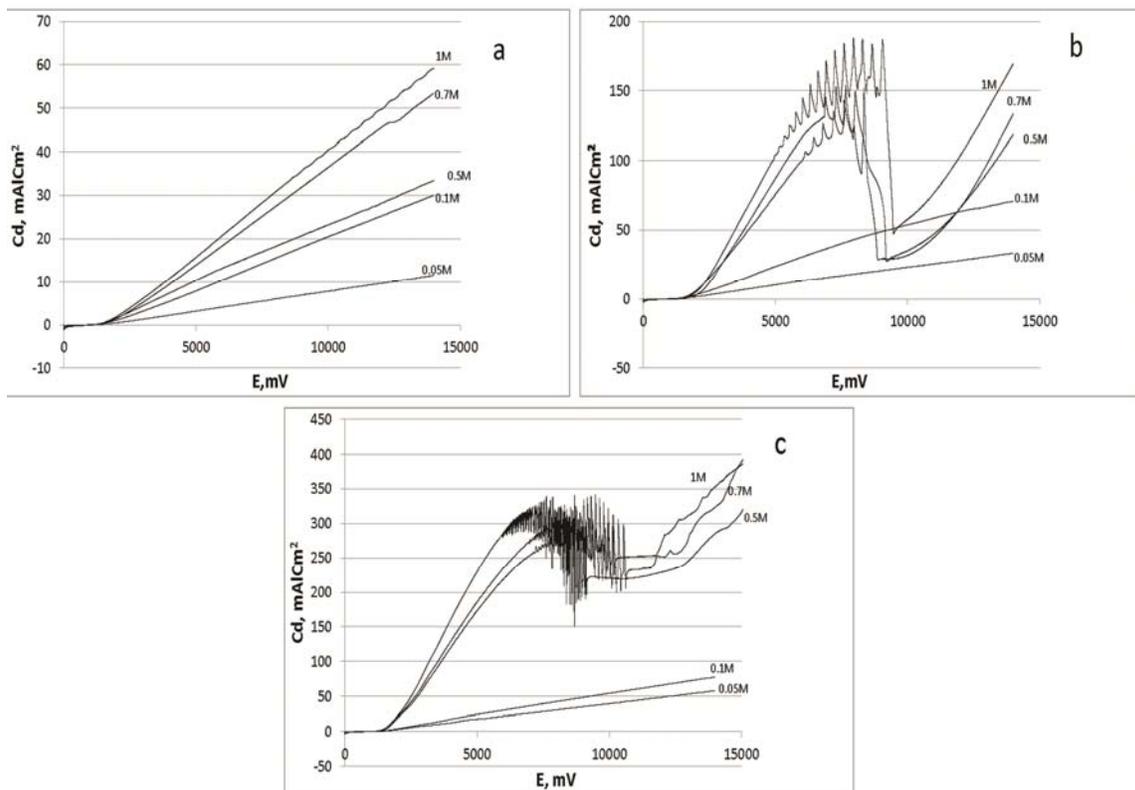


Fig (1) : Anodic and cathodic polarization curves of copper electrode in (a) MCA (b)DCA (c)TCA solutions.

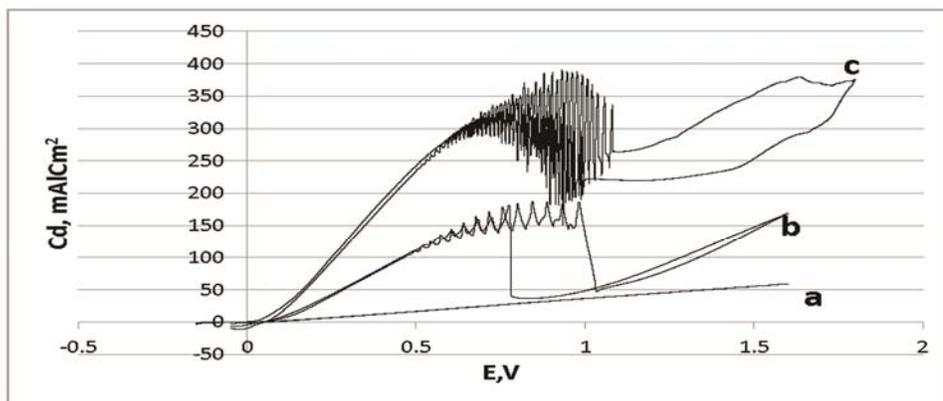


Fig (2): Cyclic voltametric curves of copper electrode in (a) MCA (b) DCA (c) TCA solutions

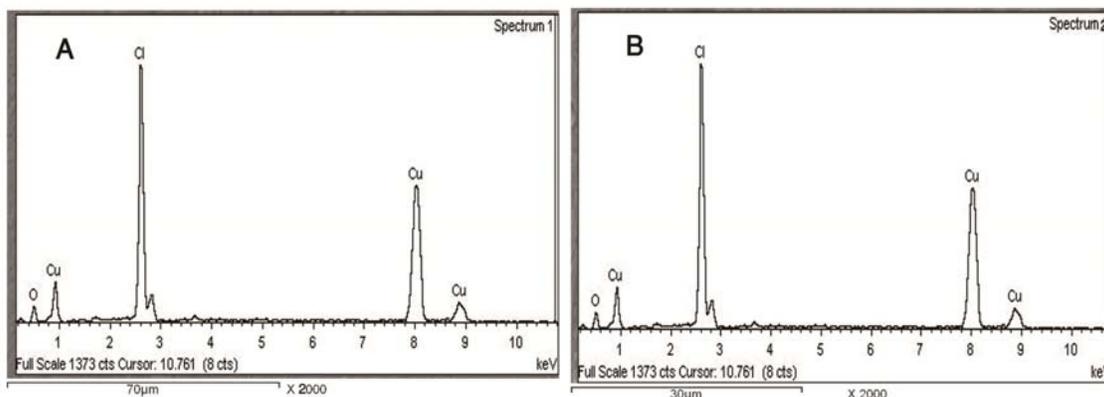


Fig.(3): EDX spectr of copper electrode in 0. 5M of (A) DCA (B) TCA solutions.

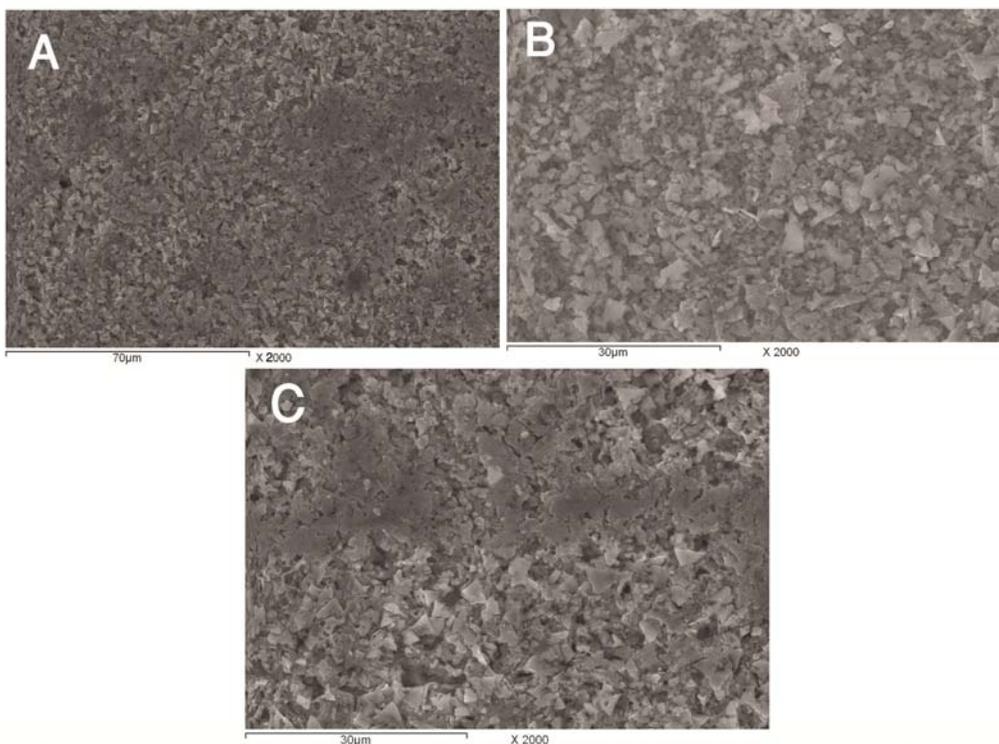


Fig.(4): Surface morphology for copper electrode in 0. 5M of (A) MCA (B) DCA (C) TCA solutions.

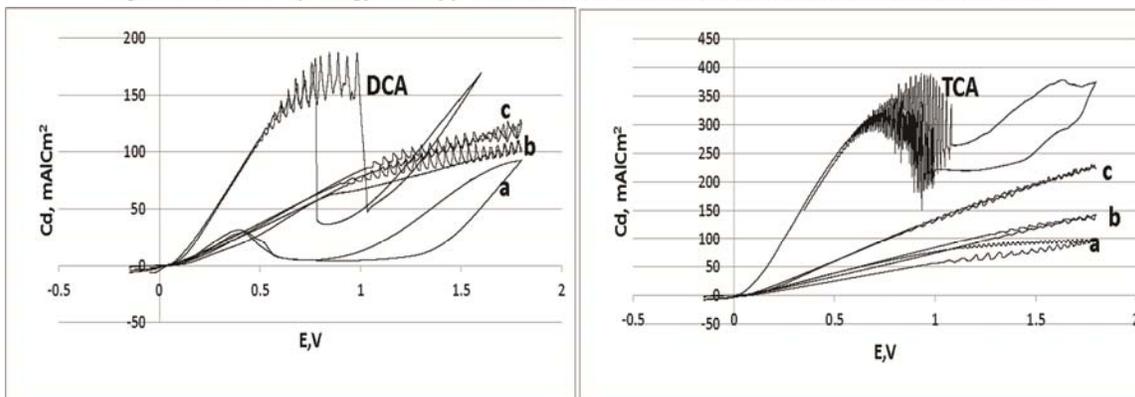


Fig (5): Cyclic voltametric curves of copper electrode in 0.5M DCA and 0.05MTCA with 0.2M(a) diphenyl alanine (b) valine (c) alanine solutions

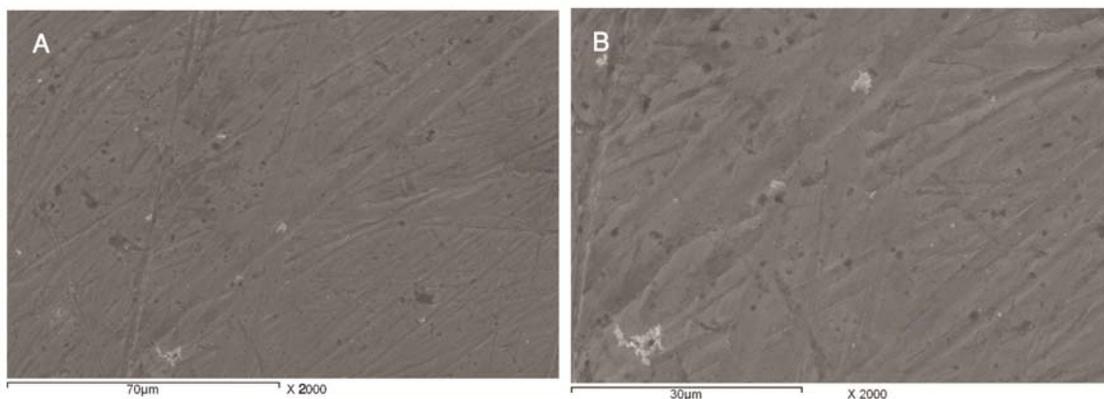


Fig.(6): Surface morphology for copper electrode in 0. 5M of (A) DCA (B) TCA with 0.2M diphenyl alanine

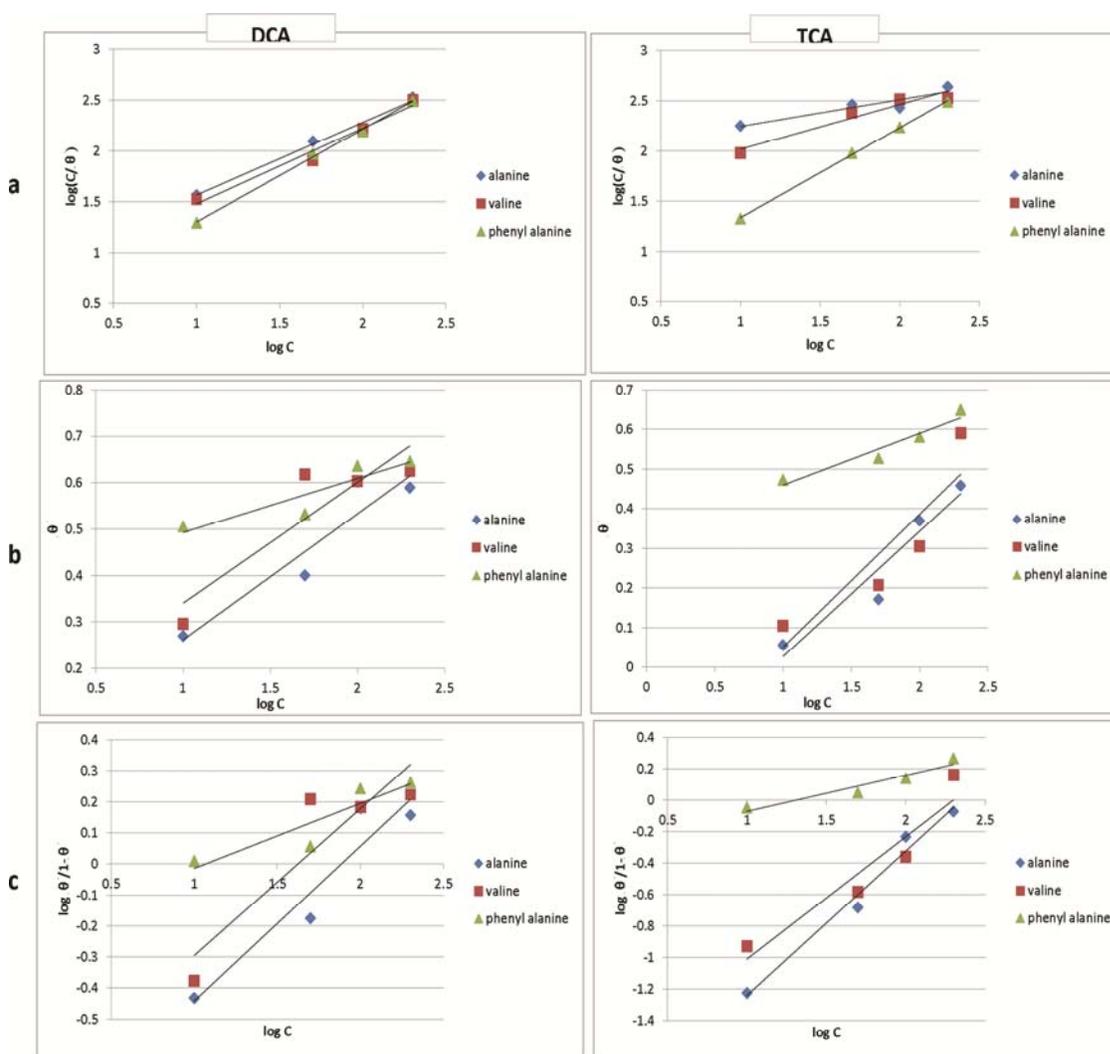


Fig.(7) Adsorption isotherms of the studied aminoacids on copper surface in 0.5M DCA and 0.5M TCA.  
 a) Langmuir b) Temkin c) kinetic thermodynamic model

**4. Conclusion:**

The following conclusion can be drawn from the investigation:

- The region of current oscillation only observed during electrodisolution of copper electrode in concentrations above 0.5M for DCA and TCA but no oscillation was observed below 0.5M and for all MCA concentrations.
- The porosity of electrode surface is in close relation with appearances of current oscillation as indicated from SEM and EDX pattern.
- Valine, alanine and phenylalanine have a retardation effect for pitting corrosion in both CU/DCA and Cu/TCA systems.
- The studied amino acids adsorbed on the copper surface according to Langmuir, Temkin and kinetic model adsorption isotherm.
- Calculated quantum parameters indicated that the trend for variation of corrosion inhibition of studied amino acids is Phenylalanine > Valine > alanine

The thing which consisted with the trend deduced from experimental results.

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**References:**

- 1 Itagaki M, M. Tagaki, K (1996), Watanabe, Study of dissolution mechanisms of copper in perchloric acid solution containing NaCl by channel flow double electrode and electrochemical quartz crystal microbalance, *Corros. Sci.* 38, 1109–1125.
- 2 Milic S.M., M.M. Antonijevic (2009), Some aspects of copper corrosion in presence of benzotriazole and chloride ions, *Corros. Sci.* 51, 28–34.
- 3 Antonijevic M.M., S.M. Milic, M.B. Petrovic(2009), Film formed on copper surface in chloride media in the presence of azoles, *Corros. Sci.* 51, 1228–1237.
- 4 Zhang D. Q., Q.R. Cai, L.X. Gao, K.Y. Lee,(2008), *Corros. Sci.* 50, 3615–3621.
- 5 Appa Rao B.V., Md. Yakub Iqbal, B.(2009), Sreedhar, Self-assembled monolayer of 2-(octadecylthio)benzothiazole for corrosion protection of copper, *Corros. Sci.* 51, 1441–1452.
- 6 Cooper J.F., R.H. Muller, C.W. Tobias (1980), Periodic phenomena during anodic dissolution of copper at high current densities, *J. Electrochem. Soc.* 127, 1733–1744.
- 7 Lee H.P., K. Nobe (1985), A.J. Pearlstein, Film formation and current oscillations in the electrodisolution of Cu in acidic chloride media. I. Experimental studies, *J. Electrochem. Soc.* 132, 1031–1037.
- 8 Pearlstein A.J., H.P. Lee, K. Nobe (1985), Film formation and current oscillations in the electrodisolution of Cu in acidic chloride media II. Mathematical model, *J. Electrochem. Soc.* 132, 2159–2165.
- 9 Bassett M. R., J.L. Hudson , The oscillatory electrodisolution of copper in acidic chloride solution I. 0.1 M chloride (1990), *J. Electrochem. Soc.* 137, 922–932.
- 10 Bassett M.R., J.L. Hudson (1990), The oscillatory electrodisolution of copper in acidic chloride solution II. 0.3 and 0.5 M chloride, *J. Electrochem. Soc.* 137, 1815–1826.
- 11 Cui Q., H.D. Dewald (2005), Current oscillations in anodic electrodisolution of copper in lithium-ion battery electrolyte, *Electrochim. Acta* 50, 2423–2429.
- 12 Kiss I.Z., V. Gáspár, L. Nyikos (1998), Stability analysis of the oscillatory electrodisolution of copper with impedance spectroscopy, *J. Phys. Chem.* 102, 909–914.
- 13 Li L., S. Chen, H. Wu, H. Cui, Chaotic (2004), mixed-mode and periodic oscillations during the electro-oxidation of copper in trichloroacetic acid, *J. Serb. Chem.Soc.* 69, 33–42.
- 14 Wahee A., M. Khaled, M. Ahlam (2006), Corrosion control of Cu–Ni alloys in neutral chloride solutions by amino acids, *Electrochimica Acta* 51, 4182–4189.
- 15 Elmorsi M.A. and A.M. Hassanein (1999), Corrosion inhibition of copper by heterocyclic compounds, *Corrosion science.* 4, 12337-2352.
- 16 Evans U.R. (1934), Metallic corrosion, passivity and protection, *B. Word Arhedd* 53,33.
- 17 Ebenso E.E., P. C. Okafor and U. J. Ekpe (2003), Studies on the inhibition of aluminium corrosion by 2-acetylphenothiazine in chloroacetic acids, 50, 414-421
- 18 LIANG LI, SHENHAO CHEN, HONGTAIWU and HAITAO CUI (2004), Chaotic, mixed-mode and periodic oscillations during the electro-oxidation of copper in trichloroacetic acid, *J.Serb.Chem.Soc.* 69(1)33–42
- 19 Waheed A. Badawy, Khaled M. Ismail , Ahlam M. Fathi (2006), Corrosion control of Cu–Ni alloys in neutral chloride solutions by amino acids, *Electrochimica Acta* 51, 4182–4189
- 20 Abdel Ghanyl N.A., A. E. El-Shenawy and W.A.M.Hussien (2011), The Inhibitive Effect of Some Amino Acids on the Corrosion Behaviour of 316L Stainless Steel in Sulfuric Acid Solution, *Modern Applied Science* . 5, 19-29

- 21 Ashassi H.-Sorkhabi, Z.Qhasemi and D.Selfzadeh (2005), The inhibition effect of some amino acids towards the corrosion of aluminum in HCl+1MH<sub>2</sub>SO<sub>4</sub> solution, Applied surface science, 249,408-418
- 22 Da-Quan Zhang, Qi-Rui Cai, Xian-Ming He, Li-Xin Gao and Guo-Ding Zhou (2008), Inhibition effect of some amino acids on copper corrosion in HCl solution, Materials Chemistry and Physics, 112, 353–358.
- 23 Fouda A.S., A.A.Al-Sarawy, F.Sh.Ahmed and H.M.El-Abbasy (2009), corrosion inhibition of aluminium 6063 using some pharmaceutical compounds, corrosion science 51, 485-492[24]Obot I.B., N.O.Obi-Eqbedi and S.A.Umoren (2009), the synergistic inhibitive effect and some quantum chemical parameters of 2,3-diaminonaphthalene and iodide ions on the hydrochloric acid corrosion of aluminum, corrosion science, 51, 276-282
- 25 Bentiss F.,M. Lebrini, M .Lagrene´e, M .Traisnel, A .Elfarouk and H. Vezin (2007), The influence of some new 2,5-disubstituted 1,3,4-thiadiazoles on the corrosion behaviour of mild steel in 1 MHClsolution: AC impedance study and theoretical approach. Electrochim Acta, 52(24):6865–72.
- 26 Bentiss F., M.Bouanis, B.Mernari , M.Traisnel , H.Vezin and M. Lagrene´e (2007), Understanding the adsorption of 4H-1,2,4- triazole derivatives on mild steel surface in molar hydrochloric acid. Appl Surf Sci; 253(7):3696–704.
- 27 Fang J, Li J.( 2002), Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides. J Mol Struct (Theochem);593:179–85.
- 28 Arslan T., F. Kandemirli, EE. Ebenso, I.Loveand H. Alemu(2009), Quantum chemical studies on the corrosion inhibition of some sulphonamides on mild steel in acidic medium. Corrosion Sci;51(1):35–47.