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# Corrosion inhibition of carbon steel in chloride solutions by some amino acids

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## ABSTRACT

The corrosion inhibition of carbon steel was investigated in stagnant naturally aerated chloride solutions using amino acids as environmentally safe corrosion inhibitors. The corrosion rate was calculated in the absence and presence of the corrosion inhibitor using the polarization technique and electrochemical impedance spectroscopy. The experimental impedance data were fitted to theoretical data according to a proposed electronic circuit model to explain the behavior of the alloy/electrolyte interface under different conditions. The corrosion inhibition process was found to depend on the adsorption of the amino acid molecules on the metal surface. Cysteine, histidine, phenylalanine and arginine have shown remarkably high corrosion inhibition efficiency. The corrosion inhibition efficiency was found to depend on the structure of the amino acids. The mechanism of the corrosion inhibition process is based on the adsorption of the amino acid molecules on the active sites of the metal surface. Results obtained from potentiodynamic polarization indicated that the inhibitors are mixed-type inhibitor.

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## 1. Introduction

Carbon steel, an alloy of iron and carbon is used in various industries because of its low cost and easy availability for fabrication of reaction vessels, girders, machine parts, rivets, tanks and pipes. Chloride ions are usually recognized as the main cause of pitting corrosion in carbon steel due to their localized nature, leading to passive layer breakdown [1,2]. The hostility of chloride ion is as a result of its size, diffusivity and strong acidic anionic nature [3]. A lot of research has been made on the corrosion behavior of steel in carbonated-chloride brine [1]. Corrosion caused by chloride can be generally reduced by using inhibitors to minimize the attack of the metal [4-13]. Various thiadiazole compounds have been assessed as good corrosion inhibitors for steel in acidic and sulfate solutions [14-20].

The most efficient corrosion inhibitors are organic compounds containing electronegative functional groups and π electrons in their triple or conjugated double bonds [21]. The initial mechanism in any corrosion inhibition process is the adsorption of the inhibitor on the metal surface [22,23]. The adsorption of the inhibitor on the metal surface can be facilitated by the presence of hetero atoms (such as N, O, P and S) as well as aromatic ring. The inhibition of the corrosion of metals can also be viewed as a process that involves the formation of chelate on the metal surface, which involves the transfer of electrons from the organic compounds to the surface of the metal and the formation of a coordinate covalent bond. In this case, the metal acts as an electrophile while the nucleophilic center is in the inhibitor. Literature reveals that wide range of compounds have been successfully investigated as potential inhibitors for the corrosion of metals [24,25]. However, a close examination of these compounds indicates that some of them are toxic to the environment while others are expensive. These and many other factors have prompted a continuing search for better inhibitors. Possibilities include plant extracts, some drugs and other natural occurring products [26-28]. It is interesting to note that amino acids are components of living organisms and are precursors for protein formation. Several researchers have investigated the inhibitory potential of some amino acids and the results obtained from such studies have given some hope for the use of amino acids as green corrosion inhibitors [29-31].

In this work some of amino acids as glycine, valine, leucine, glutamic acid, proline, aspartic acid, lysine, methionine, threonine, cysteine, histidine, phenyl alanine and arginine molecules were used as inhibitors to control the corrosion of carbon steel electrode in a 0.5 M NaCl solution. The corrosion rate and corrosion inhibition efficiency were calculated. In this respect, conventional electrochemical techniques such as potentiodynamic polarization techniques and electrochemical impedance spectroscopy (EIS) were used. Fitting of the

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experimental impedance data to theoretical values according to equivalent circuit models enables understanding of the corrosion inhibition mechanism and the suggestion of the suitable model that explains the electrochemical behavior of the alloy/solution interface under different conditions.

## 2. Experimental

The inhibitor molecules used in this paper were purchased from Sigma-Aldrich. The carbon steel electrode was prepared in the form of cylindrical rod and mounted into glass tubes of appropriate diameter by epoxy resin leaving a free surface area of 0.2 cm$^2$ to contact the solution. An all glass three-electrode electrochemical cell, with a platinum counter electrode and saturated calomel reference electrode was used. The chemical composition of carbon steel is: 0.34 C, 0.93 Mn, 0.26 Si, 0.0.2 S, 0.04 P, 0.01 Cu, 0.01 Cr, 0.02 Ni and balance Fe. The working electrode was pretreated by mechanical polishing with successive grade-emery papers up to 2000 grit, rubbing with a smooth polishing cloth, washing with triple distilled water, and then quickly transferred to the cell. All measurements were carried out in stagnant, naturally aerated neutral 0.5 M NaCl solution free or containing 10 mM of amino acids. The potentiodynamic polarization and impedance measurements were performed using an electrochemical workstation. The potentials were measured against and referred to the saturated calomel reference electrode ($E^o$ = 0.245 V the standard hydrogen electrode, SHE). The electrode potential was left in the electrolyte to achieve the steady state until the potential change did not exceed 0.1 mV/min. This potential was taken as the steady state potential, $E_{ss}$. The potentiodynamic experiments were conducted at a scan rate of 10 mV/s. The values of the corrosion potential, $E_{corr}$, and corrosion current density, $i_{corr}$, were extrapolated from the potentiodynamic polarization curves. For all EIS measurements, excitation amplitude of 10 mV peak-to-peak in the frequency range from 0.1 to 10$^5$ Hz was used. The corrosion inhibition efficiency, $\eta$, and the degree of adsorption, θ, were calculated from the values of the corrosion current densities. The experimental results were reproduced and each experiment was carried out at least twice where a good reproducibility was attained.

## 3. Results and discussion

### *3.1. Potentiodynamic polarization measurements*

The electrochemical behavior of the carbon steel was investigated by the polarization technique. Linear polarization experiments and Tafel extrapolation measurements were used. The potentiodynamic polarization curves of the electrode were recorded after 60 min of electrode immersion in 0.5 M sodium chloride solutions at a scan rate of 10 mV/s and 25 °C. In these experiments a constant concentration of 10 mM of the different amino acids was used. Figures 1 presents the potentiodynamic polarization curves obtained in the presence of different amino acids. For comparison, the polarization curve in amino acid free solution was introduced in these figures. The corrosion parameters *i.e.* the corrosion potential, $E_{corr}$, corrosion current density, $i_{corr}$, and the corrosion rate of the carbon steel in amino acid free and amino acid containing solutions are calculated and presented in Table 1. It is clear from the potentiodynamic data and Figure 2 that the presence of the amino acid decreases the corrosion rate. This is also reflected on the values of both $\beta_a$ and $\beta_b$ in most cases a decrease in these values was recorded (Table 1), which means that both the cathodic and anodic reaction rates were decreased in the presence of the amino acid molecules. The general shift of the open-circuit potential and the decrease of the $\beta_a$ and $\beta_b$ values and the current density $i_{corr}$ with the addition of inhibitors especially for phenylalanine and arginine (Figure 2). This due to that, the addition of inhibitor reduces anodic dissolution of metal and also retards evolution of oxygen reaction. This effect is due to the adsorption of inhibitor on the active centers of steel surface. The corrosion parameters, evaluated from Tafel polarization curves are listed in Table 1. From Figure 1, we can see that the shape of the different polarization curves nearly the same. This behavior suggests that the inhibitor molecules have no effect on the metal dissolution mechanism. In addition, the values of $E_{corr}$ do not change significantly in the presence of inhibitor. So, aminoacids acts as a mixed type inhibitor [32]. The corrosion inhibition efficiency, $\eta$, was calculated from the values of the corrosion current density without inhibitor, $i_{corr}$, and its value in the presence of the inhibitor, $i_{corr}$ (inh), according to:

$$\eta = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} x100 \qquad (1)$$

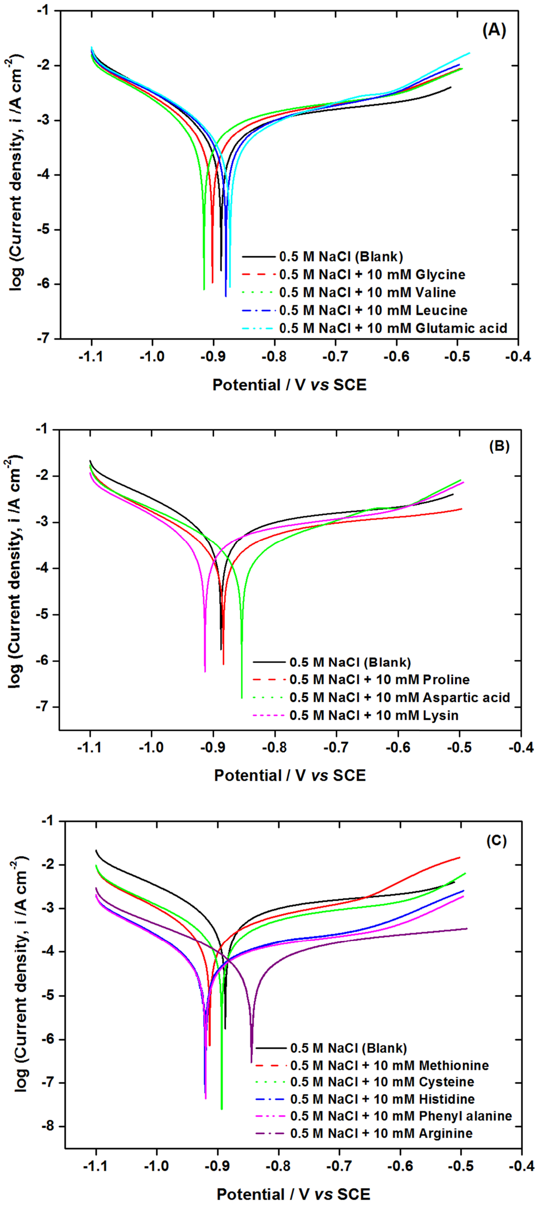

**Figure 1.** Potentiodynamic polarization curves of carbon steel after 60 min of electrode immersion in 0.5 M chloride, stagnant, naturally aerated solutions of pH = 7 using different amino acids at constant concentration of 10 mmol/dm$^3$ and 25 °C.

**Table 1.** The corrosion parameters of the carbon steel corrosion in stagnant naturally aerated neutral 0.5 M NaCl solution free and containing different amino acids at 25 °C. The surface coverage and inhibition efficiency are also presented.

| Concentration (mM/L) | $i_{corr}$ (μA/cm²) | $E_{corr}$ (mV/SCE) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | Corrosion rate mm/y | θ | Surface area (cm²) | η (%) |
|---|---|---|---|---|---|---|---|---|
| Blank 0.5 M | 229.3 | -882.5 | 239.8 | -134.5 | 2.700 | - | - | - |
| Glycine | 219.0 | -900.7 | 92.4 | -67.7 | 2.590 | 0.044 | 0.01 | 4.0 |
| Valine | 216.7 | -914.3 | 80.7 | -62.3 | 2.560 | 0.054 | 0.01 | 5.4 |
| Leucine | 171.5 | -878.6 | 75.9 | -59.8 | 2.030 | 0.252 | 0.50 | 25.2 |
| Cysteine | 96.8 | -892.3 | 94.7 | -74.5 | 1.185 | 0.578 | 0.12 | 57.8 |
| Methionine | 128.6 | -911.9 | 127.7 | -93.7 | 1.574 | 0.439 | 0.09 | 43.9 |
| Histidine | 47.5 | -920.5 | 203.6 | -112.7 | 0.582 | 0.792 | 0.16 | 79.2 |
| Threonine | 48.7 | -909.7 | 243.9 | -112.6 | 0.596 | 0.788 | 0.16 | 78.8 |
| Phenyl alanine | 27.6 | -918.9 | 119.4 | -77.4 | 0.339 | 0.879 | 0.18 | 87.9 |
| Lysine | 179.4 | -912.7 | 136.2 | -85.8 | 2.197 | 0.218 | 0.04 | 21.8 |
| Proline | 166.5 | -882.0 | 158.8 | -103.6 | 2.040 | 0.274 | 0.05 | 27.4 |
| Aspartic acid | 133.4 | -853.1 | 137.8 | -104.3 | 1.633 | 0.418 | 0.08 | 41.8 |
| Arginine | 33.1 | -843.1 | 156.4 | -116.8 | 0.405 | 0.855 | 0.17 | 85.5 |
| Glutamic acid | 182.3 | -871.3 | 86.1 | -68.8 | 2.157 | 0.209 | 0.04 | 20.9 |

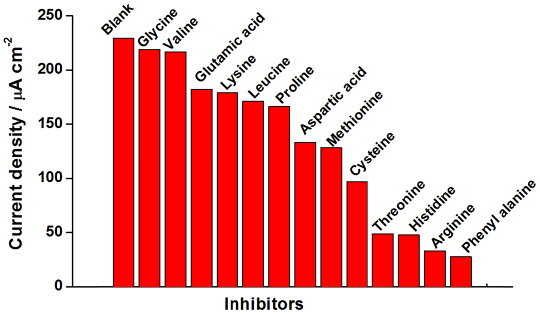

**Figure 2.** Effect of the different amino acids at constant concentration of 10 mmol/dm³ on the corrosion rate of carbon steel in stagnant, naturally aerated 0.5 M chloride solutions of pH = 7 at 25 °C.

It is clear from the values presented in Table 1 and Figure 3 that the inhibition efficiency depends on the structure of the amino acid. The presence of functional groups like OH, SH or phenyl in the backbone of the amino acid molecule increases its corrosion inhibition capability. Therefore, the calculated corrosion inhibition efficiency for such a low concentration (0.01 mol/dm³) of phenylalanine and arginine approaches more than 80%. Such high inhibition efficiency is due to the increased capability of the molecule to be adsorbed on the alloy surface by different functional groups leading to higher surface coverage which prevents the interaction between the alloy surface and the corrosive medium. Amino acids containing benzene ring like phenyl alanine or hetero ring as histidine have higher efficiency that can be attributed to the delocalized π-electrons of the aromatic system, which enables its adsorption on the metallic surface. The high inhibition efficiency of cysteine is due to the presence of the SH group. It is well known that organic corrosion inhibitors are adsorbed on metallic surfaces through hetero-atoms like nitrogen, oxygen or sulfur. The inhibiting effect follows the sequence O < N < S < P [33-35]. The presence of the -SH group in the molecular structure of cystine provokes an increase of the inhibition efficiency. The SH group is more donor and offers the possibility to be an adsorption center beside the nitrogen atom of the amino group [23]. The corrosion inhibition process is based on the adsorption of the amino acid molecules on the active sites and/or deposition of the corrosion products on the alloy surface [36]. The adsorption of aminoacids on the steel surface in 0.5 M NaCl solution may be achieved by the interaction between the unshared electron pairs of hetero atoms in aminoacids structure as O, N, and S with d-orbitals of iron atoms. The electron configuration of iron was [Ar] $4s^2 3d^6$, it is clear that, 3d orbit was not fully filled with electron. This unfilled orbital of iron could bond with the highest occupied molecular orbital of amino acids while the filled 4s orbital could interact with the lowest unoccupied molecular orbital of the inhibitor [37].

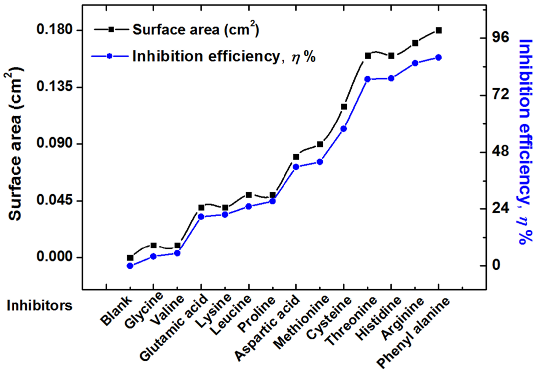

**Figure 3.** Variation of the inhibition efficiency and the surface coverage of the carbon steel after 60 min of electrode immersion in stagnant, naturally aerated 0.5 M chloride solutions of pH = 7 using different amino acids at constant concentration of 10 mmol/dm³ and at 25 °C.

It is well know that the cathodic reaction for metals and alloys in neutral solution is primarily the oxygen reduction [38]. On the other hand, the anodic reaction for iron and its alloys is the dissolution to ferrous cations and further to ferric cations [39]. It has been reported [39-42] that this dissolution is accelerated by the presence of oxygen due to the increased consumption of the produced electrons by the anodic reaction at the cathodic one. Figure 1 depicts that the steel electrode shows a passive potential region between -800 mV and -600 mV vs. Ag/AgCl as a result of the formation of passive layer of iron oxides and/or corrosion products on the electrode surface. Oh *et al.* [43] has reported that iron can develop up to nine different oxide phases on its surface; in this case the possible oxides that might form at these conditions can be represented according the following reactions [40];

$$\mathrm{Fe} + \frac{1}{2}\mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_2} \quad (2)$$

$$3\ \mathrm{Fe(OH)_2} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{Fe_3O_4} + 3\ \mathrm{H_2O} \quad (3)$$

The formed ferrous hydroxide, Equation (2), reacts with more oxygen to form the top layer of corrosion product, $Fe_3O_4$ (magnetite). The presence of such oxide partially protects the steel surface from further dissolutions and leads in turn to the appearance of a passive region on the polarization potential-current behavior. The passive region dissolves under the influence of chloride ions attack and pitting corrosion occurs as indicated by the rapid increases in the current values for steel with increasing potential. But, the presence of amino acids the effect of chloride ion decreases.

### *3.2. Electrochemical impedance spectroscopic investigations, EIS*

The results of the potentiodynamic polarization experiments were confirmed by EIS. This technique is powerful in studying corrosion mechanisms and adsorption phenomena at the electrode/electrolyte interface [44]. EIS spectra are generally displayed either in the form of Nyquist (i.e. complex plane) or Bode plots. Bode plots are recommended as standard impedance plots, since all experimental impedance data are equally represented and the phase angle, as a sensitive parameter to interfacial phenomena, appears explicitly [45-47]. The technique enables the simulation of the experimental impedance data to pure electronic models that can verify or role out mechanistic models and enables also the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation [46,48,49].

The EIS technique was applied to investigate the effect of the different amino acids on the corrosion behavior of the carbon steel in the chloride free neutral solutions. The Bode plots of the carbon steel electrodes in amino acid free solutions and in solutions containing 10 mM of the different amino acids are presented in Figure 4. In general, the phase maximum at the intermediate frequencies broadens and acquires lower values in the presence of the amino acid, which indicates the presence of passivation phenomenon [50]. The Nyquist plots shows single capacitive loop, both in uninhibited and inhibited solutions and the diameter of the capacitive loop increases after addition of inhibitor to the corrosive medium indicating that, the corrosion inhibition of steel. The whole impedance data were analyzed using software provided with the electrochemical work-station, where the dispersion formula was used. In this formula an empirical factor α (0 ≤ α ≤ 1) is introduced to account for the deviation from the ideal capacitive behavior due to surface inhomogeneties, roughness factors and adsorption effects as presented in Equation (4) [46,48-51].

$$Z = R_S + \frac{R_{ct}}{1+(2\pi f R_{ct} C_{dl})^{\alpha}} \qquad (4)$$

where $f$ is the frequency in Hz.

The experimental impedance results were fitted to a theoretical values according to a simple equivalent circuit model consisting of a parallel combination representing the electrode capacitance, $C_{dl}$, and the charge transfer (corrosion) resistance, $R_{ct}$, in series with a resistor, $R_s$, representing the ohmic drop in the electrolyte (Figure 4d). The fitting parameters were calculated for the investigated amino acids at a constant concentration of 10 mM and presented in Table 2. At a concentration of 10 mM phenyl alanine shows the highest corrosion resistance. This result is in good agreement with the results of the potentiodynamic experiments. The ranking of the four promising amino acids 10 mM, as corrosion inhibitors for the carbon steel in 0.5 M sodium chloride solutions, follows the order: phenyl alanine > arginine > histidine > cysteine.

### *3.3. Surface morphology by SEM*

SEM provides a pictorial representation of the surface. This helps to understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel. The SEM images of carbon steel specimen before and after immersion in 0.5 M sodium chloride solution for 5 h in the absence and presence of inhibitor system are shown in Figure 5. The morphology of specimen surface in the absence of inhibitor (Figure 5b) shows that, a very rough surface was observed due to rapid corrosion attack of the metal in the corrosive solution. On the contrary, in the presence of the inhibitor (Figure 5c), the rough surface is suppressed, due to the formation of an adsorbed protective film of the inhibitor on the metal surface which effectively controls the dissolution of carbon steel [42,52].

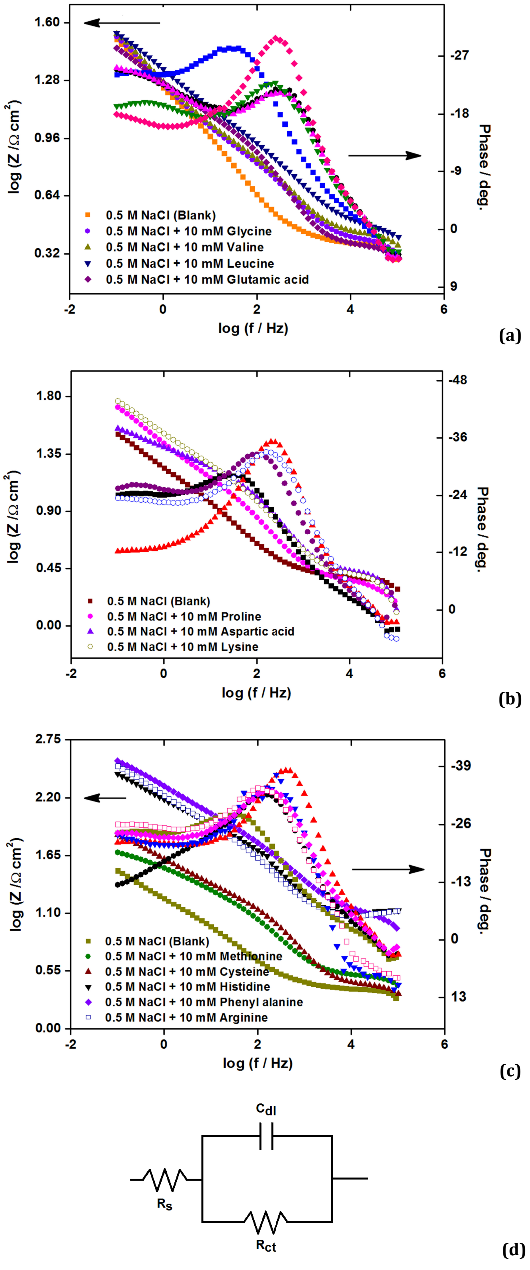

**Figure 4.** (**a-c**) Bode plots of carbon steel after 60 min of electrode immersion in stagnant, naturally aerated 0.5 M chloride solutions of pH = 7 using different amino acids at constant concentration of 10 mmol/dm³ and 25 °C. (**d**) Equivalent circuit model for impedance data fitting of the carbon steel immersed in stagnant, naturally aerated 0.5 M chloride solutions of pH = 7 containing different amino acids at 25 °C. $R_s$= solution resistance, $R_{ct}$= charge transfer (corrosion) resistance, $C_{dl}$= electrode capacitance.

## 4. Conclusion

The corrosion inhibition of carbon steel in 0.5 M NaCl solution by amino acids as an eco-friendly inhibitor has been studied using electrochemical techniques and SEM analysis.

**Table 2.** The fitting impedance parameters of the carbon steel electrode in stagnant naturally aerated neutral 0.5 M NaCl solution free and containing 10 mM/L of different amino acids at 25 °C.

| Inhibitors | $R_S$ (Ω) | $R_{ct}$ (Ω cm²) | $C_{dl}$ (μF/cm²) |
|---|---|---|---|
| Blank 0.5 M | 2.3 | 13.4 | 375.7 |
| Glycine | 2.4 | 13.8 | 1153.0 |
| Valine | 2.7 | 8.9 | 296.2 |
| Leucine | 2.8 | 13.4 | 592.7 |
| Cysteine | 2.4 | 22.7 | 175.3 |
| Methionine | 2.3 | 55.6 | 2860 |
| Histidine | 11.7 | 71.5 | 35.2 |
| Threonine | 14.7 | 72.2 | 139.2 |
| Phenyl alanine | 11.4 | 139.8 | 113.7 |
| Lysine | 2.0 | 32.5 | 979.9 |
| Proline | 2.0 | 23.7 | 1061.0 |
| Aspartic acid | 2.3 | 24.0 | 331.9 |
| Arginine | 10.7 | 119.9 | 132.6 |
| Glutamic acid | 2.2 | 10.5 | 303.1 |

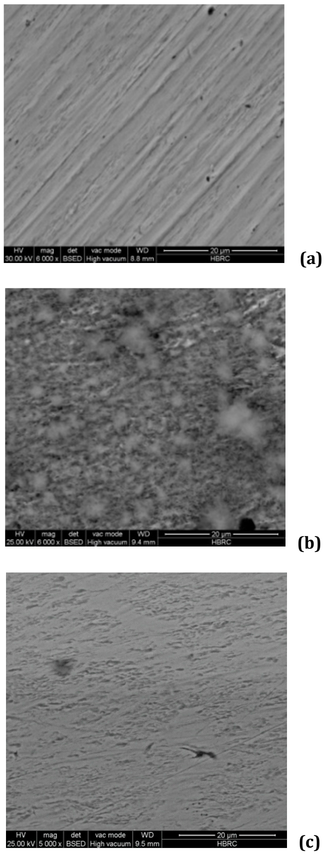

**Figure 5.** The surface morphology of polished samples before (a) and after immersion (b) in chloride solutions and (c) in presence of 10 mM of phenylalanine.

The inhibition efficiency depends on the chemical structure of amino acid. The presence of aromatic ring and hetero atoms such as sulfur in the amino acid structure causes a significant increase in the inhibition efficiency. The mechanism of the corrosion inhibition process is based on the adsorption of the amino acid molecules on the active sites of the alloy surface. Results obtained from potentiodynamic polarization indicated that the inhibitors are mixed-type inhibitor. Results obtained from all electrochemical techniques are in good agreement.

## References

[1]. Al-Kharafi, F. M.; Atea, B. G.; AbdAlla, R. M. *J. Appl. Electrochem.* **2002**, 32, 1363-1370.
[2]. Aramaki, K.; Shinura, T. *Corros. Sci.* **2006**, *48*, 209-225.
[3]. Galvele, J. R. *Corros. Sci.* **1981**, *21*, 551-579.
[4]. Bockris, J. O. M.; Yang, B. *J. Electrochem. Soc.* 1991, *138*, 2237-2252.
[5]. Bentiss, F.; Traisnel, M.; Lagrene, M. *Corros. Sci.* **2000**, *42*, 127-146.
[6]. Bouklah, M.; Hammouti, B.; Benkaddour, M.; Benhadda, J. *Appl. Electrochem.* **2005**, *35*, 1095-1101.
[7]. Elkadi, L.; Mernari, B.; Traisnel, M.; Bentiss M.; Bentiss, M. *Corros. Sci.* **2000**, *42*, 703-719.
[8]. Wang, H. L.; Liu, R. B.; Xin, J. *Corros. Sci.* **2004**, *46*, 2455-2466.
[9]. Mahmoud, S. S. *J. Mater. Sci.* **2007**, *42*, 989-997.
[10]. Fouda, A. S.; Mostafa, H. A.; Ghazy, S. E.; El-Farah, S. A. *Int. J. Electrochem. Sci.* **2007**, *2*, 182-194.
[11]. Villamizar, W.; Casales, M.; Gonzalez-Rodriguez, J. G. *J. Solid State Electrochem.* **2007**, *11*, 619-629.
[12]. Fiala, A.; Chibani, A.; Darchen, A.; Boulkamh, A.; Djebbar, K. *Appl. Surf. Sci.* **2007**, *253*, 9347-9356.
[13]. Fouda, A. S.; Abd El-Aal, A.; Kandil, A. B. *Desalination* **2006**, *201*, 216-223.
[14]. Mahdavian, M.; Ashhari, S. A. *Electrochim. Acta* **2010**, *55*, 1720-1724.
[15]. Valek, L.; Martinez, S. *Mater. Lett.* **2007**, *61*, 148-151.
[16]. Azhar, M. E.; Mernari, B.; Traisnel, M.; Bentiss F.; Lagrenee, M. *Corros. Sci.* **2001**, *43*, 2229-2238.
[17]. Lebrini, M.; Lagrenee, M.; Vezin, H.; Traisnel, M.; Bentiss, F. *Corros. Sci.* **2007**, *49*, 2254-2269.
[18]. Lebrini, M.; Bentiss, F.; Vezin, H.; Lagrenee, M. *Corros. Sci.* **2006**, *48*, 1279-1291.
[19]. Lebrini, M.; Lagrenee, M.; Traisnel, M.; Gengembre, L.; Vezin, Bentiss, H. F. *Appl. Surf. Sci.* **2007**, *253*, 9267-9276.
[20]. Bentiss, F.; Lebrini, M.; Lagrenee, M.; Traisnel, M.; Elfarouk, A.; Vezin, H. *Electrochim. Acta* **2007**, *52*, 6865-6872.
[21]. Emregu, K. C.; Duzgun, E.; Atakol, O. *Corros. Sci.* **2006**, *48*, 3243-3260.
[22]. El-Ashry, E. S. H.; El Nemr, A.; Esawy, S. A.; Ragab, S. *Electrochim. Acta* **2006**, *51*, 3957-3968.
[23]. Eddy, N. O.; Odoemelam, S. A.; Odiongenyi, A. O. *J. Appl. Electrochem.* **2009**, *39*, 849-857.
[24]. Sahin, M.; Gece, G.; KarcI, F.; Bilgic, S. *J. Appl. Electrochem.* **2008**, *38*, 809-815.
[25]. Rodriguez Valdez, L. M.; Villamisar, W.; Casales, M.; Gonzalez Rodriguez, J. G.; Martinez Villafanee, A.; Martinez, L. *Corros. Sci.* **2006**, *48*, 4053-4064.
[26]. Eddy, N. O.; Odoemelam, S. A. *Pigment Resin Technol.* **2009**, *38*, 111-115.
[27]. Eddy, N. O.; Odoemelam, S. A.; Odiongenyi, A. O. *Green Chem. Lett. Rev.* **2009**, *2*, 111-119.
[28]. Eddy, N. O.; Odoemelam, S. A.; Ekwumemgbo, P. *Sci. Res. Essays.* **2008**, *4*, 33-38.
[29]. Yurt, A.; Bereket, G.; Ogretir; C. *J. Mol. Struct. (Theochem)* **2005**, *725*, 215-221.
[30]. Ashassi Sorkhabi, A.; Shaabani, B.; Seifzadeh, D. *Electrochim. Acta* **2005**, *50*, 3446-3452.
[31]. Ashassi Sorkhabi, H.; Ghasemi, Z.; Seifzadeh, D. *Appl. Surf. Sci.* **2005**, *249*, 408-418.
[32]. El-Haddad, M. N.; Elattar, K. M. *Res. Chemic. Intermed.* **2012**, *39*, 3135-3149.
[33]. McCafferty, E. Corrosion Control by Coating, Science Press, Princeton, NJ, 1979, pp. 279.
[34]. Thomas, J. G. N. Proc. 5th Eur. Symp. Corrosion Inhibitors, Ann. Univ. Ferrara, 1981, pp. 453.
[35]. Helal, N. H.; Badawy, W. A. *Electrochem. Soc.* **2011**, *56*, 6581-6587.
[36]. Bereket, G.; Yurt, A. *Corros. Sci.* **2001**, *43*, 1179-1195.
[37]. Li, Y.; Zhao, P.; Liang, Q.; Hou, B. *Appl. Surf. Sci.* **2005**, *250*, 1245-1253.
[38]. Sherif, E. M.; Park, S. M. *J. Electrochem. Soc.* **2005**, *152*, B205-B211.
[39]. Al-Mobarak, N. A. *Int. J. Electrochem. Sci.* **2008**, *3*, 666-675.
[40]. Farelas, F.; Ramirez, A. *Int. J. Electrochem. Sci.* **2010**, *5*, 797-814.
[41]. El-Hafez, G. M. A.; Badawy, W. A. *Electrochim. Acta* **2013**, *108*, 860-866.
[42]. El-Haddad, M. N. *Carbohy. Polym.* **2014**, *112*, 595-602.
[43]. Oh, S. J.; Cook, D. C.; Townsend, H. E. Hyperfine Interactions, **1998**, *112*, 59-65.
[44]. Macdonald, J. R. Impedance Spectroscopy, John Wiley&Sons, NewYork, 1987.
[45]. Tait, W. S. An Introduction to Electrochemical Corrosion Testing for Practing Engineering and Scientists, University of Wisconsin-Madison, Racine, USA, 1994.
[46]. Badawy, W. A.; Al-Kharafi, F. M.; El-Azab, A. S. *Corros. Sci.* **1999**, *41*, 709-727.
[47]. Aouniti, A.; Khaled, K. F.; Hammouti, B. *Int. J. Electrochem. Sci.* **2013**, *8*, 5925-5943.
[48]. Hladky, K.; Calow, L. M.; Dawson, J. L. *Br. Corros. J.* **1980**, *15*, 20-25.
[49]. Hitzig, J.; Titz, J.; Juettner, K.; Lorenz, W. J.; Schmidt, E. *Electrochim. Acta* **1984**, *29*, 287-296.
[50]. Bohe, A. E.; Vilche, J. R.; Juettner, K.; Lorenz, W. J.; Paatsch, W. *Electrochim. Acta* **1989**, *34*, 1443-1448.
[51]. Cang, H.; Fei, Z.; Shi, W.; Xu, Q. *Int. J. Electrochem. Sci.* **2012**, *7*, 10121-10131.
[52]. Badiea, A.; Mohana, K. N. *Korean J. Chem. Eng.* **2008**, *25*, 1292-1299.