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Abstract

Corrosion behavior of aluminium in 0.6 mol. dm⁻³ NaCl solution in acidic medium (pH = 0.7) was investigated in the absence and presence of different concentrations of amino acid, methionine, as environmentally – friendly corrosion inhibitor over temperature range (293-308)K. The investigation involved electrochemical polarization method using potentiostatic technique and optical microscopy, the inhibition efficiency increased with an increase in inhibitor concentration but decreased with increase in temperature. Results showed that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface and it was found to obey Langmuir adsorption isotherm. Some thermodynamic parameters ($\Delta G_{ads.}$) and activation energy (E_a) were calculated to elaborate the mechanism of corrosion inhibition. The polarization measurements indicated that methionine is of mixed type. The surface characteristic of the inhibited and uninhibited metal samples were investigated by optical microscopy.

Keywords: Corrosion inhibition, Aluminium, Methionine, Adsorption Mechanism Thermodynamic parameters.



Introduction

Aluminium and its alloys have a remarkable economic and attractive materials for engineering applications owing to its low density, high thermal and electrical conductivity, attractive appearance and relatively good corrosion resistance. Alumininum is actually a very active metal, meaning that its nature to oxidize is very quickly, while a weakness for most metals; this quality is in fact the key to its ability to resist corrosion. The combination of these properties makes it a preferred choice for many industrial applications such as automobiles, aviation, aerospace, food handling, containers, electronic devices, buildings, etc^[1].

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is constant and has continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination^[2].

Corrosion of metal is caused by electrochemical reaction between a metal (or an alloy) and aqueous phase. It proceeds according to a complex electrochemical process that is related to the atomic structure of matter. The corrosion of metal is the result of two simultaneous reactions that are in electrical equilibrium, i.e. oxidation of metal to ions and reduction of hydrogen to hydrogen gas ^[3].

Hydrochloric acid and sulphuric acid solutions are used for pickling of aluminium or for its chemical or electrochemical etching. It is very important to add corrosion inhibitors to decrease the rate of metal dissolution using organic compounds. It is known that the organic compounds are effective corrosion inhibitors due to their ability to form an adsorbed protective film at the metal surface^[3,4].

Unfortunately, most of the inhibitors available in the markets are not only expensive but also toxic to living beings. Again, the safety of environmental issues of corrosion inhibitors which may be arise industry has always been a global concern^[5].

To avoid toxicity of numerous compounds tested as inhibitors^[6,7], natural compounds, regarded as environmentally friendly inhibitors. Amino acids have been tested as inhibitors of corrosion of a variety of metals, for example copper, aluminium and steel corrosion in acid media. They are relatively easy to produce with high purity at low cost, non-toxic and soluble in aqueous media^[6,7].

In the present work, the inhibitive effectiveness of amino acid (methionine), have been studied in retarding corrosion of aluminium in $0.2M\ H_2SO_4$ by use of electrochemical polarization measurements. Furthermore, this study aim to throw some light on the role of the functional groups of the inhibitors used in the adsorption process as well as the influence of the nature of the medium on the corrosion mechanism.

Optical microscopy was employed to observe the surface morphology of the aluminium corroded in test solution.



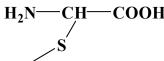
2. Experimental part

2.1 Materials

The experiments were performed with aluminium sheets (99.8% purity) of 2mm thickness, which was mechanically press-cut into circular form 2cm diameter.

All chemicals and reagents used are with analytical grade and use without further purification, they include:

- a. Sodium chloride, was used for preparation of the aggressive solution of 0.6 $mol\ dm^{-3}$.
- b. Sulphuric acid.
- c. The amino acid (L-Methionine) tested as inhibitor (>99% purity). Its structure is shown below.



2.2. Solution

The aggressive solution used was made of A.R. Sodium chloride to prepare $0.6mol\ dm^{-3}$ concentration in pH=0.7. Doubled distilled water was used for the preparation. For each experiment a freshly solution was made. Three concentrations of the inhibitor (methionine) were used $(10^{-3}, 5 \times 10^{-3}\ and\ 10^{-2})mol\ dm^{-3}$.

2.3 Potentiostatic polarization measurements

The polentiostatic polarization measurements were carried out with aluminium sheets (explained before) having an exposed surface area of $1cm^2$ to corrosive medium [in absence and presence the inhibitor].

The open side of the working electrode (aluminium sheet) was grinded and polished mechanically using wheel machine. All samples were grinded via a series grades of emery papers [100, 200,400,800,1200 and 2000] and polished with smooth cloth to a mirror finish. The specimen were degreased with acetone and thoroughly washed with distilled water then dried and kept in a desicator until use.

Polarization measurements were performed in a three electrodes cell with aluminium specimen of $1cm^2$ exposed area, a platinum electrode and silver-silver chloride in saturated KCl solution were used as working, auxiliary (counter) and reference electrodes respectively.

The measurements were carried out using M lab potentionstat / Galvanostat 200 Germany obtained from Bank Electronic Intelligent Controls Gnb H. It was connected to personal computer desktop the Mlab software cares for controlling the potentiostat, recording and processing data. It provides electrochemical calculations like Tafel line evalution, re-scalling the potential and integrating.

The experiments were preformed in $0.6mol\ dm^{-3}\ NaCl$ solution of (pH=0.7) in absence and presence of three different concentrations of the inhibitor (methionine) over the temperature range (293-308)K. The experiments were carried out at a scan rate of 2mV/s.

Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were determined from the polarization curve, in addition other informations were obtained such as Tafel slopes $(b_c \ and \ b_a)$ weight loss and penetration values. In order to test the reproducibility of the results, the experiments were done in triplicate.

3. Results and Discussion

3.1 Tafel polarization measurements

The effect of 0.6 mol. dm⁻³ NaCl solution in acidic medium on the corrosion of aluminium sample was studied using Tafel polarization technique. Figure 1 represents the potentiostatic



polarization curves of aluminium at four temperature in range of (293-308)K. Corrosion parameters such as corrosion potential (E_{corr}) , corrosion current density (i_{corr}) , anodic slope (b_a) and cathodic slope (b_c) are obtained from the Tafel polarization curves. Results are tabulated in Table 2.

The results indicate the increase in the corrosion current density (i_{corr}) with an increase in

The negative shift in the corrosion potential (E_{corr}) with the increase in temperature indicates that the anodic process is much more affected than the cathodic process, this observation is in accordance with other published results^[1,2] which proposed the dependence of (i_{corr}) and (E_{corr}) on solution parameters. The change in (b_a) and (b_c) reflects the mechanism of corrosion process.

The electrochemical cathodic and anodic reactions of aluminium in acidic solution can be described as follows[8].

$$AL + H_2O \rightarrow ALOH_{(ads)} + H^+ \tag{1}$$

$$AL + H_2O \rightarrow ALOH_{(ads)} + H$$

$$ALOH_{(ads)} + 5H_2O + H^+ \rightarrow Al^{3+} + 6H_2O + 2e^+$$

$$AL^{3+}H_2O \rightarrow [ALOH]^{2+} + H^+$$
(3)

$$AL^{3+}H_{2}O \rightarrow [ALOH]^{2+} + H^{+}$$
 (3)

$$[ALOH]^{2+} + X^{-} \rightarrow [ALOHX]^{+} \tag{4}$$

Thus soluble complex ion formed leads to the dissolution of the metal.

3.2 Effect of Temperature

The effect of temperature on the corrosion rate of aluminium (expressed by i_{corr}) was studied by measuring the corrosion at the temperature range of (293-308)K. The dependence of the corrosion current density (i_{corr}) on temperature followed Arrhenius equation^[9].

$$rate(r) \equiv i_{corr} = A \exp(-E_a/RT)$$
 (5)

which can be expressed in logarithmic form:

$$\ln i_{corr} \equiv \ln A - \frac{E_a}{RT} \tag{6}$$

Where A and E_a are repectively the pre-exponential factor and the activation energy of corrosion reaction.

A typical linear plot relating values of $\ln i_{corr}$ to the reciprocal of temperature $\left(\frac{1}{\tau}\right)$ as shown in Figure 2 was obtained.

The values of E_a could be derived from the slope of the line, and when the linear plot of Figure 2 was extrapolated to $\ln i_{corr}$ value at $\left(\frac{1}{T}\right) = 0$, the value of A could be obtained.

Table 3 represents the values of E_a , ΔS^* and the pre-exponential factor (A) for aluminium sample in (pH = 0.7).

Entropy of activation (ΔS^*) was calculated from the value of (A) using the relationship:

$$A = \frac{kT}{h} \exp \frac{\Delta S^*}{R} \tag{7}$$

were (k) is boltzman constant, (h) is Plank constant, (R) is the universal gas constant and (T) the absolute temperature of the solution [10,11].

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The entropy of activation is negative, this implies that activated complex in the rate determining step represents association than dissociation, indicating that a decrease in disorder takes place, in going from reactants to the activated complex.

Figure 3 shows the typical polarization curves of aluminium in $0.6mol\ dm^{-3}\ NaCl$ solution containing three different concentrations of amino acid (Methionine) as a green inhibitor over the temperature range (293-308)K. Table (4) presents the polarization data ($E_{cor}\ and\ i_{corr}$) and from these data it can be noticed that the addition of methionine caused a decrease in corrosion current densities of aluminium, the inhibition effect of methionine increases as the concentration of the inhibitor increases in the range $(10^{-2}-10^{-3})mol\ dm^{-3}$ at all temperatures of study.

Table (5) shows the values of inhibition efficiencies (IE%) which were calculated from equation(8):

$$IE \equiv \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \tag{8}$$

Where i_{corr}^0 and i_{corr} are corrosion current densities in absence and presence of the inhibitor respectively.

3.3: Corrosion Inhibition of Aluminum\\ by Methionine

The essential effect of corrosion inhibition is because of the presence of electron donor groups (S,N,O) in the molecular structure of the Methionine. It is well known that the presence of heteroatoms, for nitrogen, oxygen and sulfur in the inhibitor structure results in better inhibition [12]. Also the most organic substance employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms. Its inhibition efficiency should follow the sequence O < N < S [13]. Electron pairs on the heteroatoms can be shared with metal orbitals, forming an insoluble complex that protect the surface from the aggressive ions by blocking of its corrosion sites and hence decreasing the corrosion rate [14]. The presence of pairs of free electrons on sulfur, nitrogen and oxygen atoms favours adsorption of methionine and, thus, the best efficiency of this inhibitor.

The activation parameters such as activation energy (E_a^*) and the entropy of activation (ΔS_a^*) in the range of the studied temperatures (293-308)K for corrosion inhibition of aluminium in 0.6 $mol\ dm^{-3}\ NaCl$ solution in the presence of various concentrations of methionine were calculated using Arrhenius equation:

$$rate \equiv i_{corr} = A \exp\left(\frac{-E_a}{RT}\right) \tag{9}$$

The calculated values E_a^* and ΔS_a^* are summarized in Table (6). In the presence of the inhibitor, an increase in E_a^* values were observed, the variation of activation energy E_a^* in the presence of different concentrations of methionine can be illustrated as follows^[15]: higher values of (E_a^*) were found in presence of the inhibitor than those without inhibitor, i.e., the addition of methionine raise the energy barrier for the corrosion process of aluminium in chloride acid solution^[16].

It was found that there is a direct relation between the values of (E_a) and A, i.e. simultaneous increase or decrease in (E_a) and $\ln A$ for a particular system which can be ascribed to the compensation effect which describes the kinetics of catalytic and tarnishing reaction on the metal.

The entropy values of activation, ΔS_a^* , in the presence of methionine are negative implying the rate determining step for the activated complex which is the association rather than



dissociation step, in addition the adsorption process is accompanied by an increase in entropy which is the driving force for the adsorption of methionine on to the aluminium surface^[17].

3.4: Thermodynamic Parameters of The Adsorption Isotherm

The efficiency of organic compounds as good corrosion inhibitors depends mainly on their adsorption ability on the metal surface. Basic information about the interaction between inhibitor and metal can be provided by the adsorption isotherm. The investigation of the relation between corrosion inhibition and adsorption of inhibitor is of great importance.

The surface coverage Table (7) and the concentration of methionine solution (c_{meth}) were tested by fitting to various isotherms like: Langmuir, Tempkin and freundlich.

However, the fit was obtaind with Langmuir isotherm as shown in Figure (4) which is given by the following equation^[18].

$$\frac{C_{met}}{\theta} = \frac{1}{k_{ad}} + C_{met} \tag{10}$$

Where k_{ads} is the equilibrium constant of the adsorption / desorption process, and it reflects the affinity of the inhibitor molecules towards surface adsorption sites.

From the intercepts of the straight lines on the C_{met}/θ axis Fig (4) leads to the equilibrium constant for the adsorption / desorption of methionine process, Table (8). The high value of K_{ads} reveals that the methionine molecule possesses strong adsorption ability on to the aluminium.

However, k_{ads} decreased with an increase of temperature indicating that adsorption of methionine on to the metal surface was favorable at lower temperatures.

The equilibrium constant of the adsorption / desorption (k_{ads}) was related to the standard free energy of adsorption according to the equation.

$$\Delta G_{ads}^0 = -RTm(55.5 k_{ads}) \tag{11}$$

Where R is the universal gas constant, T is the absolute temperature, and (55.5) is concentration of water in solution.

The standard free energy of adsorption was calculated and is given in Table (8). Generally the standard free energy of adsorption values $-25kJ.mol^{-1}$ or less negative are associated with an electrostatic interaction between charged metal surface or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond. So it can be concluded that adsorption of methionine on to aluminium surface takes place through both physical and chemical adsorption^[19].

From Table (4) it was clearly seen that the presence of methionine reduces the corrosion rate of aluminium in sulphuric acid solution. As its well known that different substituents on the organic molecules polarize the functional group in a different manner^[11]. This indicates that the protective effect of methionine is not solely due to their reactivity with sulphuric acid in acidic media, NH_2 of amino acid molecule is readily protonated to form NH_3^+ . Also the addition of amino acids with aliphatic radical R leads to decrease corrosion current density but when the radical contains heteroatom as N,O or S a decrease of corrosion current densities in the presence of methionine at 10^{-3} , 5×10^{-3} and 10^{-2} mol. dm^{-3} was noted.

 E_{corr} shifts to little more negative values in the presence of methionine tested-as shown in Table (7).

This result indicates that the inhibitors have been adsorbed to both cathodic and anodic areas. That means methionine is mixed type inhibitor. The same results have been reported by other authers^[20,21].



Then the addition of amino acids molecules in sulphuric acid solution seems that no effect on anodic behavior is observed. This result shows that the inhibitory action of these compounds depends on the potential for higher E_{corr} potential inhibitory character disappears.

It is generally accepted that the first step in the adsorption of methionine on the metal surface usually involves the replacement of one or more water molecules adsorbed at the metal surface^[22].

$$Meth_{(soln)} + H_2O_{ads} \rightleftharpoons Meth_{ads} + H_2O_{(soln)}$$
 (12)

The inhibitor methionine may then combine with freshly generated Al^{+3} ions on the aluminium surface, forming metal inhibitor complex^[23]

$$Al \rightarrow Al^{+3} + 3e$$
 (13)
 $Al^{+3} + Meth_{ads} \rightarrow [Al - Meth]_{ads}$ (14)

$$Al^{+3} + Meth_{ads} \rightarrow [Al - Meth]_{ads} \tag{14}$$

Valuable information about the mechanism of corrosion inhibition can be provided by the values of thermodynamic parameters for the adsorption of inhibitor. Thermodynamically, ΔG_{ads}^0 were related to the standard enthalpy, ΔH_{ads}^0 and standard entropy, ΔS_{ads}^0 according $to^{[8]}$.

$$\Delta G_{ads}^0 = \Delta H_{ads}^0 - T \Delta S_{ads}^0 \tag{15}$$

 $\Delta G_{ads}^0 = \Delta H_{ads}^0 - T \Delta S_{ads}^0 \tag{15}$ And the standard enthalpy of adsorption can be calculated on basis of the Van't Hoff formula:

$$\ln K_{ads} = -\frac{\Delta H_{ads}^0}{RT} + constant \tag{16}$$

A plot of $\ln k_{ads}$ vs. 1/T gives a straight line as shown in Fig (5). The slope of straight line is

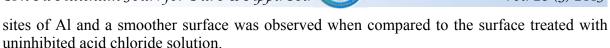
The negative sign of ΔH_{ads}^0 reveals that the adsorption of inhibitor molecules is an exothermic process. Generally, an exothermic adsorption process suggests either physisorption or chemisorption while endothermic process is attributed to chemisorption. The unshared electron pairs in investigated molecules may interact with P-orbitals of aluminium to provide a protective chemisorbed film^[16].

The values of ΔS_{ads}^0 in the presence of inhibitor are negative that is accompanied with exothermic adsorption process. ΔS_{ads}^0 of inhibitor can be calculated from equation (8) according to^[8] following formula.

$$\Delta S_{ads}^0 = \frac{\Delta H_{ads}^0 - \Delta G_{ads}^0}{T} \tag{17}$$

3.5: Optical Microscopy Observation

The surface morphology of Aluminium specimens exposed to acid chloride solution in absence and presence of methionine for two hours was examined by optical microscope technique. Figure (6) showed the image of Aluminium surface which immersed in the aggressive solution with and without the addition of 10^{-2} mol. dm⁻³ of methionine. It can be observed that the specimen surface was strongly damaged in absence of inhibitor due to metal dissolution in the aggressive solution. A number of pits distributed over the surface are seen Figure (6c). However, no pits and cracks were observed in the micrograph after the addition of inhibitor to the aggressive solution Figure (6b). Inhibitor molecules adsorbed on active



References

- 1. Nasim ziaifer, Jila talatmehrabad and farzad arjomendirad (2011). "Aluminium corrosion inhibitors in Acidic Media", J.Basic Appl. Sci. Res, 1(12) 2886-2888.
- 2. Sahaya. A. Raja, Rajendean, S.; Sathiyabama, J. and Angel P. (2014). "Corrosion control by Aminoactic acid (Glycine) an over view, international Journal of Innovatine Research in science, Engineering and Technology. 3, 4, 11455-11467.
- 3. Panchal, V.A.; Patel, A.S.; Trivedi, P.T. and Shah, N.K. (2012). "Corrosion Inhibition of AL-Mg alloy in hydrochloric acid using Benzylamine N. (P-methoxy benzylidene" J. Mater. Environ. Sci 3(2) (360-373).
- 4. Musa, A.Y.; Mohamad, A.B.; Kadhumand, A.A.H., and Tabal, Y.B.A. (2011) "Inhibition of Aluminium Alloy corrosion in 0.5*M* nitric acid solution by 4-4-Dimethyloxalidine-2-thione Journal of mater. Engin. and per for, 20(3), 294.
- 5. Ingrid Milosev, Jasminka Pavlinac, Milan Hodosceek And Antonija Lesar (2013). "Amino acids as corrosion inhibitors for copper in acid medium: Experimental and theoretical study" J. Serb. Chem. Soci. 78(12) 2069-2086.
- 6. Ashassi-Sorkhabi, H.; Ghasemi, Z., and Scifzadeh, D. (2005). "The inhibition effect of some amino acids towards the corrosion of aluminium in 1M HCl+1M H₂SO₄ solution", Applied surface science 249, 408-418.
- 7. Zhang, D.Q.; Cai, Q.R.; He, X.M.; Gao, L.X. and Kim, G.S. (2009). "Corrosion inhibition and adsorption behavior of methionine on copper in HCl and Synergistic effect of zinc ions", materials chemistry and physics, 114 (612-617).
- 8. Deepa Prabhu and Padmalatha RaO (2014). "Corrosion behavior of 6063 aluminium alloy in acidic and in alkaline media" Arabian Journal of chemistry, (1-9).
- 9. Murgulesen, L.G. and Rdovi, O. (1961). "metal corrosion", Int. congr. 10-5 April, London, 202-205.
- 10. Zarrouki, A.; warad. I. and Hamouti. B. (2012), "Kinetic Parameters of Activation, int, J. Electrochem. Sci, 5, 1516-1526.
- 11. Trowsdale, A. J.; Nabel, B.; Harris, S.J.; Gibbins, I.S.R.; Thompson, G.E. and Wood, G.C., (1996). "The influence of silicon carbide reinforcement on the pitting behavior of aluminium" corros. Sci. 2, 177-191.
- 12. Mihit., M.; Bazzi, L.; Salghi. R.; Hammouti B.; elissami S. and Ait adds., E. (2008). "Some tetrazolic compounds as corrosion inhibitors for copper in nitric acid medium" int. Sci. Althern. Energ. Ecology 62, 173.
- 13. Moretti, G.; Guidi ,F. (2002) "Tryptophan as copper corrosion inhibitor in 0.5 M aerated sulfuric acid' Corros. Sci. 44, 1995.
- 14. khaled, K.F.; fadl-Allah., S.A. and Hammouti., B. (2009) ""some benzotriazole, drivatives as corrosion inhibitors for copper in acidic medium: experimental and quantum chemical molecular dynamics approach" Materials chemistry and physics 117 148-155.
- 15. Barouni, K.; Kassale, A.; Albourine, A.; Jbara, O.; Hammouti, B. and Bazzi L. (2014). "Amino acids as corrosion inhibitors for copper in nitric acid medium: Experimental and theoretical study" J.Mater. Environ. Sci. 5(2), 456-463.
- 16. Aplya, S.; Fakrudeen, P.; Ananda murthyh, C. and Bheema Ratu. V., (2012). "Corrosion Inhibition of AA 6061 and 6063 Alloys in Hydrochloric Acid Medium by Schiff base compound", Journal of the Chilean chemical Society, 57, 4, 1364-1370.
- 17. Fouda, A. S.; Shalabi, K. and Mohamed. N.H. (2014). "Corrosion Inhibition of aluminium in Hydrochloric Acid solutions using some chalcone derivatives" international J. of innovative research in science, engineering and technology, vol 3, 9861-9875.
- 18. Kliskic, M.; Radosevic, J. and Gridic. S.(1997). "Pyridine and its derivatives as inhibitors of aluminium corrosion in chloride solution". J. Appl. Electrochem.. 27, 947-952.



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- 19. Ghongli, X.; Deng., Sh. and Huifu (2011). "Sodium molbydate as corrosion inhibitor for aluminium in H_3PO_4 solution J. corrosion science. 53 (2748-2753).
- 20. Achutha kini, U.; Prakash Shetty, Divakara Shetty, S. and Arun Isloor., M. (2011). "Corrosion inhibition of 6061 AA/SiCp composite in hydrochloric acid medium using. 3-chloro-1-benzothiophene-2-carbohydrazide". 18, 439-445.
- 21. Sorkhabi, A.; Majidi, H. and Seyyedi., M.R., K. (2004). "investigation of inhibition effect of some aminoacids against steel corrosion in HCl solution", Applied surface science, 225 (1-4), 176-185.
- 22. Lebe Nnanna, A.; Onyinyechi, Nwadiuko, C.; Nneka ekekwe., D.; Chibneze ukpadi., F., Solomon udensi., C., Kelechukwu okema., B., Beniah onwugba., N. and Ihebrodike mejeha M. (2011). "Adsorption and inhibitive properties of leaf exract of new bouldia leavis as Green inhibitor for Aluminium Alloy in H_2So_4 ", American Journal of materials science 1(2), 143-148.
- 23. Shrier., L.L. (1976). "Over potential, corrosion Metal/ Environments Reactions", Newnes, Butterworths, Boston, 1, 35.

Table (1): The chemical composition of pure aluminium

Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ga	V
0.07	0.2	0.05	0.05	0.001	-	-	0.009	ı	0.005

Table (2): Data of polarization curve for corrosion of pure aluminium in 0. 6 $mol. dm^{-3} NaCL$ solution at pH(0.7) over the temperature range (293-308)K.

T/K	i /u/1 am -2	$-E_{corr}/mv$	-bc/mv	ba/mv	Weight loss/	Penetration
1/1	$i_{corr}/\mu A. cm^{-2}$		decade-1	decade-1	$g.m^{-2}.day^{-1}$	loss/mm.year ⁻¹
293	129	634	528.3	47.1	10.3	1.4
298	163	678	777.6	44.2	13.1	1.78
303	203	696	303.1	44.5	16.3	2.21
308	326	739	195.9	64.7	26.2	3.55

Table (3): Activation energy (E_a) , pre-exponential (A) and entropy of activation (ΔS^*) for pure aluminium corrosion in 0.6 $mol.dm^{-3}$ NaCL solution in pH0.7.

$E_a/kJ.mol^{-1}$	$-\Delta S^*J.K^{-1}.mol^{-1}$	A/molecule cm^{-2} . S^{-1}
44.86	57	$60230000000 \times 10^{23}$



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Table (4): Values of (E_{corr}, i_{corr}) with different concentrations of methionine at temperature range (293-308) K in pH0.7

T/K	Inhibitor conc. $mol. dm^{-3}$	$-E_{corr}/mv$	i _{corr} /μA.cm ⁻²
	0	634	129
202	1×10^{-3}	667.9	59.98
293	5×10^{-3}	630	54
	1×10^{-2}	624	43.73
	0	678	163
200	1×10^{-3}	654	82.44
298	5×10^{-3}	654	74.75
	1×10^{-2}	622	58
	0	696	203
202	1×10^{-3}	645.9	103.66
303	5×10^{-3}	685	94
	1×10^{-2}	654	76
	0	739	326
200	1×10^{-3}	674	179.96
308	5×10^{-3}	688	171
	1×10^{-2}	678	131.7

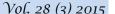




Table (5): Values of inhibitor efficiencies (IE%) calculated from i_{corr} . For pure aluminium in pH0.7

Conc. of methionine	T/K	IE% from i_{corr} .
	293	53.6
1×10^{-3}	298	50
1 × 10 -	303	49
	308	45
	293	58.2
5×10^{-3}	298	54.2
5 x 10 -	303	53.7
	308	48
	293	66.2
1×10^{-2}	298	64.5
1 × 10 -	303	62.6
	308	60

Table (6): Activation energy (E_a) , pre-exponential factor (A) and entropy of activation (ΔS^*) for the corrosion of pure aluminium in the pH value 0.7 in 0.6 $mol.dm^{-3}$ NaCL solution and different concentrations of L-methionine.

Conc.of L-methionine mol. dm ⁻³	$E_a/kJ.mol^{-1}$	$-\Delta S^*J.K^{-1}.mol^{-1}$	A/molecule $cm^{-2}.S^{-1}$
1×10^{-3}	45.96	52.25	95458116980×10 ²³
5×10^{-3}	48.83	48.45	169751204000×10 ²³
1×10^{-2}	51.7	37.62	6023000000×10 ²³

Table (7): Chosen corrosion parameter, degree of surface coverage and corrosion inhibition efficiency for pure aluminium in $0.6mol.\,dm^{-3}\,NaCL$ solution in pH=0.7 with different concentrations of methionine at various temperature.

T/K	conc. Meth. $mol. dm^{-3}$	$-E_{corr}/mv$	$i_{corr}/\mu A.cm^{-2}$	θ	IE%
	0	634	129	-	
293	1×10^{-3}	667.9	59.98	0.53	53.6
293	5×10^{-3}	630	54	0.58	58.2
	1×10^{-2}	624	43.73	0.66	66.2
	0	678	163	-	-
298	1×10^{-3}	654	82.44	0.50	50
298	5×10^{-3}	654	74.75	0.54	54.2
	1×10^{-2}	622	58	0.64	64.5
	0	696	203	-	-
303	1×10^{-3}	645.9	103.66	0.49	49
303	5×10^{-3}	685	94	0.53	53.7
	1×10^{-2}	654	76	0.62	62
	0	739	326	-	-
308	1×10^{-3}	674	179.96	0.45	45
300	5×10^{-3}	688	171	0.48	48
	1×10^{-2}	678	131.7	0.60	60



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Table (8): Equilibrium constant adsorption / desorption, standard free energy, enthalpy and entropy of adsorption onto pure aluminium in $0.6mol.dm^{-3}$ NaCL solution in pH = 0.7 in the presence of methionine at various concentrations.

T/K	$k_{ads} mol^{-1}$	$-\Delta G_{ads}^{0}kJ$. mol^{-1}	$-\Delta H_{ads}^0 kJ.mol^{-1}$	$-\Delta S_{ads}^{0} J. mol^{-1}. K^{-1}$
293	1666.7	26.75		180.03
298	1428	27.20	26	178.83
303	1111	27.70	26	177.23
308	1000	28.12		175.7



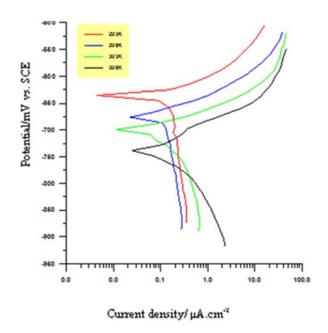


Fig. (1): Polarization curves of pure Al corrosion in pH=0.7 with (0.6 mol.dm⁻³) NaCl solution at four temperatures in the range of (293-308)K.

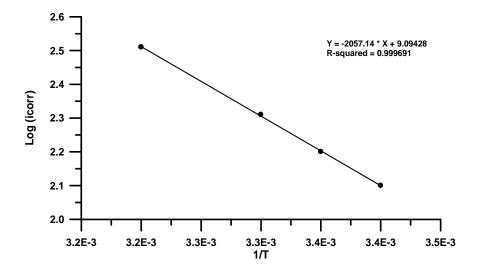


Fig. (2): Arrhenius Plot relating Log (i_{corr}) to 1/T for the corrosion of pure Al in the pH = 0.7 in presence of (0.6 mol.dm⁻³) NaCl over the temperature range (293 – 308) K.



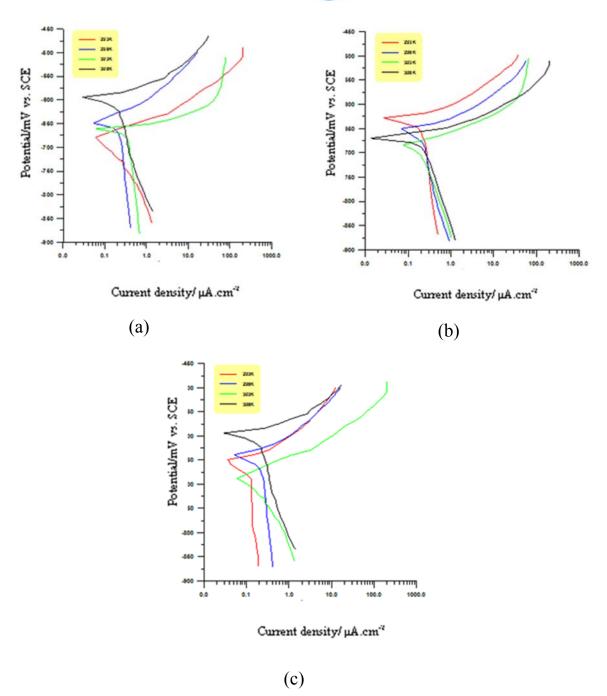


Fig. (3): The typical polarization curves of pure Al in with (0.6 mol.dm⁻³) NaCl solution containing of L-methionine as inhibitor (a= 1×10^{-3} , b = 5×10^{-3} , c = 1×10^{-2} mol.dm⁻³) over the temperature rang (293-308)K.



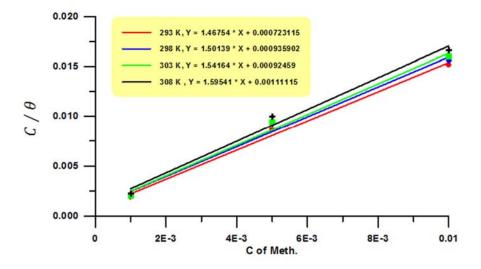


Fig. (4): Langmuir adsorption plots of L-methionine on the pure Al in 0.6 mol.dm⁻³ NaCl solution at various temperature.

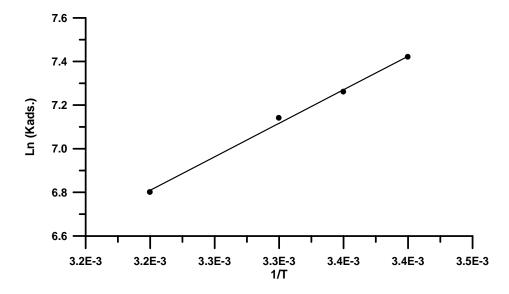
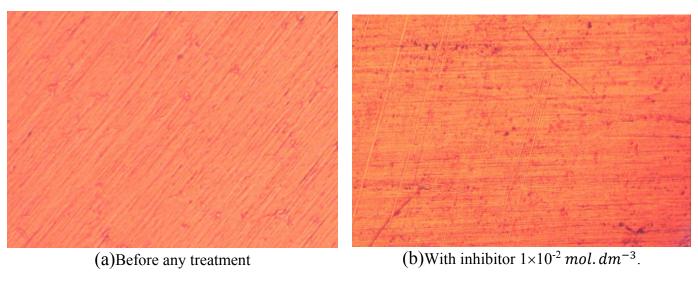


Fig. (5):Van't Hoff plot pure Al in 0.6 mol. dm^{-3} NaCl solution containing L-methionine in pH = 0.7





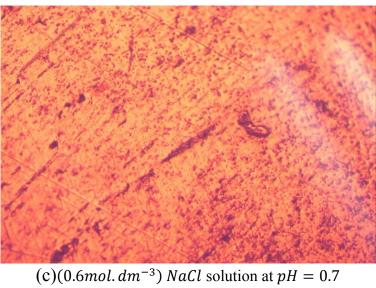


Fig. (6): Typical microstructure of pure aluminium in the corroded medium at =0.7 , magnification power $400\times$



اعاقة تآكل الألمنيوم في المحيط الحامضي باستعمال الحامض الاميني المثيونين

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الخلاصة

يتناول موضوع البحث دراسة كهروكيميائية لسلوك تآكل الالمنيوم في محلول حامضي (pH=0.7) لكلوريد الصوديوم بتركيز ($0.6mol.dm^{-3}$) بغياب ووجود تراكيز مختلفة من الحامض الاميني المثيونين كمثبط صديق للبيئة على مدى درجات الحرارة (293-308K) كما اشتملت الدراسة على طريقة الاستقطاب الكهروكيميائي باستعمال جهاز المجهاد الساكن والمجهر الضوئي.

وجد ان كفاءة التثبيط تزداد بزيادة تركيز المثبط لكنها تقل بزيادة درجة الحرارة. اظهرت النتائج ان التثبيط يحدث من خلال المتزاز جزيئات المثبط على سطح الفلز (الالمنيوم) ووجد بأنها تتبع مسار درجة الحرارة للامتزاز للانكمير (Isotherm for Adsorption). وقد تم حساب بعض المعلمات الثرموديناميكية (ΔE_a) وطاقة التنشيط (mixed type لتوضيح ميكانيكة تثبيط التآكل. قياسات الاستقطاب اوضحت بأن المثيونين مثبط من النوع المختلط (optical microscope).

الكلمات المفتاحية: الالمنيوم، المثيونين، ميكانيكية تثبيط التأكل ، المعلمات الثر موديناميكية.