Corrosion Inhibition of Aluminum Alloy 7613 by Dimethylethanolamin in (0.6 M) NaCl Solution

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ABSTRACT
The inhibition behavior of Dimethylethanolamin (DMEA) on corrosion 7613 Aluminum alloy in 0.6 M NaCl solution have been investigated using weight loss, polarization techniques. Five different concentrations ($2 \times 10^{-3}$, $4 \times 10^{-3}$, $6 \times 10^{-3}$, $8 \times 10^{-3}$, and $10 \times 10^{-3}$) M of (DMEA) were studded at 25°C. Also examine of temperature effect (25, 35, 45)°C on the inhibitor efficiency. The results indicated that the inhibition occurs by absorption of inhibitor molecules on the metal surface. The inhibition efficiency ($I\%$) was found to increase with increasing inhibitor concentration and decreasing with increasing temperature. For inhibitor concentration close to ($8 \times 10^{-3}$ M) maximum inhibition efficiency obtained was 92%. Above this inhibitor concentration value in the solution the inhibitor efficiency decreases.

Polarization measurements showed that the DMEA act as a mixed type inhibitor. The corrosion potential ($E_{corr}$) values shifted to less negative values by increasing the concentration of DMEA in the solution up to ($8 \times 10^{-3}$ M). Adsorption of DMEA on the surface of Aluminum is found to obey the Langmuir isotherm.

Keywords: Al-alloy7613, Corrosion inhibition, Dimethylethanolamin (DMEA), adsorption.
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NOMENCLATURE

Al  Aluminum
DMA  Dimethylethanolamin
C   Inhibitor concentration
Cl  Chloride ion
E   Potential (V)
E_{corr}  Corrosion potential (V)
I   Inhibitor efficiency
K   Adsorption equilibrium constant
M   Molarity
mm  Millimeter
mv  Mille volt
R   Corrosion rate (mm/year)
t   Immersion time
REMS  Rare earth metal salts
W_{1}, W_{2}  The weight loss of Al-alloy in absence ; presence of inhib., or respectively

θ   The degree of surface coverage
PVP  Polyvinyl Prrolidone
PA  Polyaclamide
REMS  Rare earth metal salt

INTRODUCTION

Aluminum alloys have been widely used in a variety of industry fields due to their favorable strength-to-weight and corrosion resistance properties. In practical aluminum alloys have been broadly integrated into vehicular heat exchanger systems, aluminum alloys are prone to corrosion even in fully inhibited coolants [1]. Aluminum has a nature corrosion protection from its oxide layer, but if exposed to aggressive environments it may corrode [2]. Aluminum and its alloys, however, are reactive materials and are prone to reaction. Owing to its wide applicability in industrial and everyday life, the electrochemical properties of aluminum and its alloys are the subject of many studies [3]. The most important problem in this area of research is related to the protection of aluminum and its alloys against corrosion. One of the most important methods is to use inhibitors.

Corrosion of aluminum & its alloys may occur through the oxide film by ionic migration followed by dissolution at the oxide/electrolyte interface [4]. Several...
attempts were made to develop a generator functioning in saline or acidic media, but in such condition, the kinetics of aluminium dissolution are reduced by the presence of quite a thick oxide-hydroxide film at the anode surface [5]. This protective film can only be broken by the presence of chloride ions in the solution or by the action of strong alkaline solution [6].

The protection of metals alloys against corrosion can be achieved either by special treatment of the medium to depress its aggressive or by introducing into a small amount of substance called corrosion inhibitors [7]. A corrosion inhibitors is a material that attaches or coats the metal surface, providing a protective barrier film, which in turn stops the corrosion reaction [8].

Inhibitors slow corrosion process by either:
- Increasing the anodic or cathodic polarization behavior (Tafel slopes)
- Reducing the movement or diffusion of ions to the metallic surface
- Increasing the electrical resistance of metallic surface

Organic and inorganic compounds are wildly used as corrosion inhibitors to control the dissolution of the protective oxide film on the surface of aluminum in alkaline solution, in order to minimize metal loss and the conception of the alkaline solution [9, 10].

Rare earth metal salts (REMS) compounds studied as a corrosion protection of commercial aluminum alloys by F. Mansfeld [11] (REMS) compounds which are non-toxic inexpensive have been used successfully for corrosion inhibition of aluminum alloys. The resistance to localized corrosion of aluminum alloys such as Al2024, Al6061 and Al7075 has been greatly improved by immersion in hot cerium salt solutions. Cerium oxides/hydroxides were formed at sites where intermetallic compounds containing copper were located and eliminated the formation of local cathodes. Bethen et al [12,13] observed, from weight loss, that lanthanum; cerium and samarium chlorides are effective uniform corrosion inhibitors of AA5083 in aerated 3.5% NaCl solution.

Neil and Garrad [14] studied the effect of Cerium pre-treatment on AA6061 prior to immersion in 3.5% NaCl solution. The effect of triethanolamine (TEA) on aluminum and (AlMgSi alloy) in 3.5% NaCl was studied by Metikos and Z. Grubac [15], using potentiodynamic and electrochemical impedance spectroscopy technique, addition of (TEA) caused decrease in the cathodic current without effecting the anodic polarization behavior. Pyridine and its selected derivatives have been studied as corrosion inhibitors for high purity aluminum in 2M NaCl solution using d.c polarization techniques by M. Kliski and Rudosovic [16], it was found that the derivatives are adsorbed on aluminum according to the freundlich isotherm.

Berkovic et al [17] studied effects of natural compound as corrosion inhibitors of aluminum and its alloys; found that the efficiency of the corrosion inhibitor by rutin and quercetin solution was the result of forming protective film on metal surface, therefore the diluted rutin and quercetin solution could be used as corrosion inhibitor of aluminum. Elamngo et al [18, 19] reported that self-
The corrosion rate of 375 aluminum alloy in 2 M NaOH is decreased as the amount of polyaniline is increased in the solution. The inhibition mechanism of corrosion of natural oxide film-covered pure aluminum by NO$_3^-$ and SO$_2^-$ ions has been examined in 0.1 M NaCl solution by Pyun et al [20] using potentiodynamic polarization experiments. It was found that NO$_3^-$ ions can be incorporated into natural oxide film on pure aluminum at open circuit potential but the incorporation of SO$_4^-$ ions into the film hardly occur. The incorporation of NO$_3^-$ ions lowered the pitting susceptibility of pure aluminum in 0.1 M NaCl solution. Irfan et al [21] studied the effects of the CeCl$_3$ concentration ions with and without addition of NaCl .PH-values of conversion solution ,time and temperature of immersion on the Ce-conversion coating form corrosion protection of sicp/5A06 Al-MMC and 5A06 Al-alloy in 3.5%NaCl at 25°C .The best corrosion resistance effects are obtained for the samples treatment in CeCl$_3$.7H$_2$O/3.5NaCl solution at 45°C and 60 minutes followed by drying at 100°C for 30 minutes this behavior due to the precipitation of Ce-oxide /hydroxide on the cathodic intermetallics and the Al-oxide film on the rest of the metal matrix.

Umoren et al [22] studied the corrosion and inhibition behavior of aluminum in hydrolic acid (HCl) in the absence and presence of (PVP),(PA) and there blends in the temperature range of (30-60) °C using weight loss hydrogen evaluation and thermodynamics technique .He reported that the inhibitor efficiency (%I) increased with increasing the inhibitors concentration and increasing temperature leads to increased the corrosion rate but decreased the inhibition efficiency ,PVP was found to have the higher in inhibition efficiency than PV which may suggest that the difference in their molecular structure play a significant role in the adsorption and hence inhibition process ,optimum efficiency was obtained at 3:1 blending ratio for PVP:PA

**EXPERIMENTAL PROCEDURE**

**Material:** The working electrodes were prepared from aluminum alloy 7613 in the form of disks with diameter of (2.5 cm) and thickness of (0.3 cm), with chemical composition of:

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Zn</th>
<th>Pb</th>
<th>Ti</th>
<th>Sn</th>
<th>V</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>92.35</td>
<td>3.64</td>
<td>1.82</td>
<td>0.8</td>
<td>0.51</td>
<td>0.34</td>
<td>0.3</td>
<td>&lt;0.2</td>
<td>&lt;0.07</td>
<td>.082</td>
<td>0.0</td>
<td>0.14</td>
<td>.007</td>
<td>&lt;0.01</td>
</tr>
</tbody>
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The corrosion medium was a 0.6 M NaCl solution of (99.8% NaCl purity) (RIEDEL-DE HAEN/GERMANY) in contact with air maintained at 25°C, Dimethylethanolamin (DMEA) supplied by (SEELZE-HANNOVER/GERMANY) with 108.14 molecular weight.
Corrosion Inhibition of Aluminum Alloy 7613 by Dimethylethanolamin in (0.6 M) NaCl Solution

Dimethylethanolamin (DMEA)

Were added at a concentrations of \( (2 \times 10^{-3}, 4 \times 10^{-3}, 6 \times 10^{-3}, 8 \times 10^{-3}, \text{and} \ 10 \times 10^{-3}) \) M

**Surface preparation:** The surface of specimens was polished down to fine emery paper with (500,800,and 1000) mesh grinding degreased with acetone, rinsed under running water and finally dried between two filter papers.

**Weight loss determination:** The weight loss (gm) was determined by weighting the samples before and after immersion for (24 hr) in 100 ml of 0.6 NaCl solution with and without addition of different concentrations \( (2 \times 10^{-3}, 4 \times 10^{-3}, 6 \times 10^{-3}, \text{8} \times 10^{-3}, \text{and} \ 10 \times 10^{-3}) \) M of Dimethylethanolamin (DMEA). After the test, the pieces were removed, washed with distilled water, dried as before and weighted again. The weight loss of the metal in the corrosive solution is given by:

\[
\Delta W = W_1 - W_2
\]

The variations of weight loss were recorded.

**Polarization test:** An electrochemical cell with capacity of 1000 ml used with three electrodes, aluminum alloys 7613, Platinum foil and reference electrode normal calomel.

Polarization measurements of specimens immersed in the NaCl solution with an exposed area of \( (19.65 \text{ cm}^2) \) at room temperature were made using a Winking LT-87/potentiostat with scan rate of 1mV/sec in the applied potential of 0.5 V (vs. SCE) to 0.9 V with respect to \( E_{\text{corr}} \).

**RESULTS AND DISCUSSION**

**Weight Loss Measurement:** Figure (1) shows the weight loss as a function of the aluminum alloy 7613 corrosion in (0.6 M) NaCl solution in absence and presence of different concentration of Dimethylethanolamin (DMEA) at room temperature. It decreases (significantly) with increasing the concentration of the DMAE in the solution so the addition of DMEA to the solution leads to reduction in the amount of material loss from the aluminum surface. Thus, the corrosion rate of aluminum alloy 7613 in 0.6 NaCl solution decrease with increasing the concentration of DMEA. This trend result from the adsorption amount and the coverage of DMEA film on the aluminum surface which increase with increasing of DMEA concentration in the solution. The corrosion rate of aluminum alloy was obtained from the following equation:

\[
R \ (\text{mm/year}) = 87.6 \ \frac{w}{D \ A \ t} \\
\]

\[ \text{......... (2)} \]
Where \( w \) is the weight loss in mg, \( D \) is the density in g/cm\(^3\), \( A \) is the area of the specimen in inch\(^2\) and \( t \) is the exposure time in hr.

**Inhibitor efficiency:** The inhibitor efficiency (\( % \ I \)) was obtained from the following equations: [25]

\[
% \ I = [1-(W_2/W_1)]\times 100\%
\] ……… (3)

From figure (2) it can be seen that the inhibitor efficiency of DMEA for Al-alloy in 0.6 M NaCl solution is a function of DMEA concentration. It was observed that the inhibitor efficiency increases with increasing the DMEA concentration, the optimum value of DMEA inhibitor efficiency was (92%) obtained at DMEA concentration of (8*10\(^{-3}\) M). Thus due to the corrosion inhibition efficiency of DMEA is related to its molecules adsorption mechanism [26]. Adsorption depends on the nature and the state of the metal surface, the type of corrosion medium and the chemical structure of the inhibitor [27].

**degree of surface coverage:** (\( \theta \))

The degrees of surface coverage (\( \theta \)) for different inhibitor concentrations were evaluated from the weight loss data and from the following equation, [25]

\[
\theta = \frac{1%}{100}
\] …….. (4)

The adsorption isotherm is often shown to demonstrate the performance of organic adsorbent – type inhibitors. Figure (3) shows the adsorption isotherm plot of DMEA on the surface of aluminum alloy 7613 in 0.6 M NaCl solution a straight line which was obtained when \( C/ \theta \) plotted against \( C \) and correlation coefficient (\( R^2 =0.992 \)). A plot suggestion that the adsorption of DMAE on the aluminum surface follows the Langmuir isotherm for the following equation:

\[
\frac{C}{\theta} = \frac{1}{K} + C
\] ……… (5)

**Corrosion inhibition mechanism**

The mechanism of the inhibition process of the corrosion inhibitors under consideration is mainly the adsorption one; the adsorption process occurred either physically or chemically. The adsorption of organic inhibitors mainly depends on some physiochemical properties of the molecules related to its functional groups. Adsorption is supposed also to depend on the possible interaction of P-orbital of the inhibitor with d-orbital of the surface atoms, which induce greater adsorption on the inhibitor molecules onto the surface of the metal leading to the formation a corrosion protection film [28].

The mechanism of corrosion inhibition using DMEA inhibitor is the adsorption of DMEA molecules on the surface of Al-alloy metal, which blocks the metal
surface and thus do not permit the corrosion process. The adsorption among the adsorbed molecules themselves as well as their interaction with the metal surface. This behavior agrees with the report by Slavcheva et al. [29, 30], where the corrosion inhibition is obtained by the adsorption onto the aluminum surface blocking the corrosion process similar to the case of sodium benzoate and phosphate [31, 32].

**Effect of inhibitor dose**

From figure (4) it can be observed that the dose effect of DMEA on corrosion efficiency for 7613 aluminum alloy in 0.6 M NaCl medium, decreases with increasing the inhibitor efficiency to higher extent, till reaches the maximum value around \(8 \times 10^{-3} \text{ M}\). The dose equals to \(8 \times 10^{-3} \text{ M}\) of DMEA considered as a critical dose of inhibition. On the other hand from figure (4) it also observed that a further increasing in the concentration of DMEA (more than \(8 \times 10^{-3} \text{ M}\)) cause a decreasing in the inhibitor efficiency, thus due to the breakdown of the protective film on the Al-alloy surface so this layer has an energy contribute for carrying the layer on the metal surface an augmentation layers will be formed on the Al-alloy surface with more additions of DMEA in the solution, so at some points on the metal surface the energy cannot loaded these addition layers, then the layers will be flawed these leads to a contact between the Al-alloy surface and the corrosion medium so an increasing of corrosion rate occurs due to chloride attack towards these flawed area.

**polarization measurement**

Polarization curves of Al-alloy 7613 in 0.6 M NaCl solution in absence and presence of different concentration of DMEA at room temperature are illustrated in figure (5). From this figure it can be observed that in absence of DMEA in the solution, the corrosion potential of aluminum alloy 7613 was \(-720 \text{ mV}\) vs. SEC. The addition of DMEA to the solution shifts the corrosion potential \(E_{\text{corr.}}\) to less negative values (shifted toward positive direction).

It is clear from this figure that the corrosion current density \(i_{\text{corr.}}\) shifted toward the left direction (to less current density) with increasing the concentration of DMEA in the solution. Figure (5) also shows that increasing the concentration of DMEA in the solution which leads to shift both anodic and cathodic branches of polarization curves to lower values of current density indicating the inhibition of both hydrogen evaluation and aluminum dissolution reaction, this indicates that the DMEA inhibitor acts as a mixed-type inhibitor.

The presence of DMEA inhibitor in the solution decreases the offensive of Cl ions towards the aluminum surface; this is due to the adsorption of DMEA molecules on the aluminum surface and protects it from the Cl ions attack [32]. The corrosion potential \(E_{\text{corr.}}\) shifted to more negative value and the corrosion current density \(i_{\text{corr.}}\) increases too that is because of increasing the concentration of DMEA inhibitor more than \(8 \times 10^{-3} \text{ M}\) in the solution so that contribute of breakdown the protect film which is covered the aluminum surface so it will be a new chloride attack towards the flawed area, indicating increase in reaction rate DMEA.
Effect of temperature on the Inhibition Process

The effect of temperature on the corrosion behavior of Al-alloy 7613 in 0.6 M media was studied by weight loss methods at different temperature in the range 25-45 °C in the absence and presence of different concentrations of DMEA and the inhibition efficiency plot vs. concentration of DMEA with different temperature figure(6), it is observed from this figure that inhibition efficiency decreases with increasing the temperature. This is due to the reduction of the adsorption inhibitor molecules (DMAE) on the surface of aluminum by increasing temperature and then the acceleration of the dissolution process [34], which is due to the fact that the rate of corrosion of Al-alloy is higher than the rate of DMEA molecules adsorption on Al surface.

CONCLUSIONS

The present study leads to the following conclusions:
1. DMEA is an effective inhibitor for the corrosion of aluminum 7613 alloy in 0.6 M NaCl solution.
2. The inhibition efficiency increases with increase the concentration of DMEA in the solution up to concentration equal to (8*10^{-3} M).
3. 92% inhibition efficiency was obtained at concentration of DMEA (8*10^{-3} M).
4. The inhibition is due to the adsorption of DMEA on the surface of aluminum.
5. The adsorption of DMEA on the surface of aluminum follows Langmuir adsorption isotherm.
6. Polarization measurements show that the DMEA function acts as a mixed-type inhibitor and the corrosion potential (E_{corr}) values are shifted to less negative values by increasing the concentration of DMEA in the solution.
7. The inhibitor efficiency decreases with increase the temperature of the solution.

REFERENCES

[22] Umoren, S. A. and E. Ebenso "Blends of Polyvinyl pyrrolidone and Polycrylamide as Corrosion Inhibitors for AL.
Corrosion Inhibition of Aluminum Alloy 7613 by Dimethylethanolamin in (0.6 M) NaCl Solution

Figure (1) Weight loss curve for the corrosion of 7613 aluminum alloy in 0.6 M NaCl solution in the absence and presence of different concentration of DMEA

Figure (2) Dependence of inhibition efficiency (I%) on the concentrations of DMEA in the solution
Corrosion Inhibition of Aluminum Alloy 7613 by Dimethylethanolamin in (0.6 M) NaCl Solution

Figure (3) Langmuir adsorption models on the 7613 aluminum alloy surface by DMEA in 0.6 M NaCl solution with $R=0.992$

Figure (4) Inhibitor efficiency as a function of DMEA concentration for 7613 aluminum in 0.6 M NaCl solution
Corrosion Inhibition of Aluminum Alloy 7613 by Dimethylethanolamin in (0.6 M) NaCl Solution

Figure (5) Polarization curves for the corrosion of 7613 aluminum alloy in 0.6 M NaCl solution in absence and presence of different concentration of DMEA.

Figure (6) Variation of inhibition efficiency (I %) with the concentration of DMEA at different temperature, for 7613 aluminum alloy in 0.6 M NaCl solution.