Aluminium corrosion inhibition using benzene-1,2,4,5-tetracarboxylic dianhydride (PMDH)

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Abstract

Purpose – The purpose of this paper is to study the inhibitory activity of benzene-1,2,4,5-tetracarboxylic dianhydride (PMDH) on aluminium corrosion in hydrochloric acid 1 M HCl.

Design/methodology/approach – The inhibitive effect of PMDH towards the corrosion of aluminium in 1 M HCl solution is studied by means of electrochemical impedance spectroscopy, polarization curves (LSV) and scanning electron microscopic techniques. The effect of inhibitor concentration and temperature against inhibitor action is investigated.

Findings – In the presence of inhibitor (PMDH), the corrosion resistance of aluminium is improved and the corrosion rate and corrosion current are reduced, therefore the inhibition efficiency and polarization resistance are increased. With increasing temperature and decreasing inhibitor concentrations, the rate of aluminium corrosion increased. The surfactant acts as mixed type inhibitor and obeys a Langmuir isotherm.

Originality/value – The results shown in this paper are an insight to the understanding of the corrosion resistance and electrochemical behaviour of aluminium for future industrial applications and development.

Keywords Metals, Corrosion inhibitors, Electrochemistry, Surface treatment

Paper type Research paper

1. Introduction

Aluminium is the most commonly used metal in power transmission and the metallurgy of non-ferrous metals due to its high-electrical conductivity, good working and forming properties, low density, lightness, ease of recycling, high-mechanical strength and ductility (Rosliza et al., 2008). Hydrochloric acid solutions are used for pickling, and chemical and electrochemical etching of aluminium. Although aluminium has a protective oxide film, which contributes to its resistance to corrosion to a great variety of chemical agents, (Shreir et al., 1994) corrosion inhibitors should be used to improve its corrosion resistance because, according to the Pourbaix diagram, the solubility of the oxide film increases below pH 4. Several authors (Rosilza et al., 2008; Shreir et al., 1994; Bagotsky, 2006; Scully, 1975; Ovari et al., 1988; Tomcsanyi et al., 1989; Stevanovic et al., 1988; Rozenfeld, 1981) have reported that the most efficient corrosion inhibitors are organic compounds that contain mainly nitrogen, sulphur or oxygen atoms in their structures. The electrons in aromatic ring and electron pairs on the hetero atoms can be shared with aluminium orbitals forming insoluble complex that protect the surface from the aggressive ions. This adsorption can be physical or chemical adsorption. Inhibitors can modify the anodic or cathodic reactions, or even both at the same time. The inhibitors efficiency depends on conditions such as temperature, strength of bonding to the metal substrate, the surface charge, the nature of the metal and the mode of adsorption of the inhibitor (Bentiss et al., 1999; Quraishi and Sardar, 2003; Bilgic and Sahin, 2001). The aim of the present investigation was to determine the inhibition efficiency of PMDH by using electrochemical techniques and investigate the effect of temperature on its efficiency in 1 M HCl solution. A chemical structure of PMDH is shown in Figure 1.

2. Methodology

2.1 Test materials

A pure aluminium (99.999 per cent) disc working electrode with a diameter of 5 mm was used in this work. All chemicals were of analytical grade. The concentration range of the inhibitor was 0.01 M to 0.0004 M in 1 M HCl.

2.2 Total immersion tests

The working electrode before each measurement was polished with emery papers from 600 to 1,200 grit sizes. Then the polished aluminium was immersed in 1 M NaOH to remove the abrasive dust on the electrode surface, degreased with acetone, washed with doubly distilled water, and finally dried before being immersed in the solution. Solutions were prepared with double distilled water and de-aerated by bubbling pure nitrogen gas for 30 min before experiments. Experiments were always repeated at least three times until a good reproducibility of the results was obtained. The effect of temperature on corrosion inhibition of PMDH was investigated at four different temperatures.

2.3 Electrochemical tests

Electrochemical experiments were carried out using AUTOLAB model PGSTAT 30. The experiments were performed in a conventional three electrodes electrochemical cell at 25°C with a platinum counter electrode and a saturated calomel reference electrode; the tip of which was very close to the surface of the working electrode to minimize the IR drop.
The open circuit potential was recorded after 30 min immersion of working electrode in the test solution, and then the impedance measurement and the potentiodynamic test was carried out.

In the polarization method, the potential was scanned in the range of $+350$ to $-350$ mV with scan rate of 1 mV s$^{-1}$. The frequency range for electrochemical impedance spectroscopy (EIS) measurements was $1 \text{kHz} \leq f \leq 0.01 \text{Hz}$. Before each experiment, the working electrode potential was kept for 3 min at $-1,200$ mV. In this way, the oxide layer was removed from the aluminium surface.

3. Results

3.1 Electrochemical impedance spectroscopy

The Nyquist plots for aluminium in 1 M HCl solution with and without PMDH in the concentration range of 0.01-0.0004 M at 25°C are shown in Figure 2.

The impedance parameters were calculated from the analysis of these diagrams are given in Table I. Values of polarization resistance ($R_p$) were calculated from the difference in real impedance at the lower and higher frequencies. Double layer capacitance ($C_{dl}$) was calculated from the maximum imaginary component of the impedance ($-Z_{max}$) from the following equation:

$$f(-Z_{max}) = \frac{1}{2\pi C_{dl} R_p}$$

(1)

where $(-Z_{max})$ is the maximum imaginary component of the impedance and the inhibition efficiency (IE per cent) is calculated by the following equation (Abd El Rehim et al., 2004):

$$\text{(IE percent)} = \frac{R_p - R_{p(\text{inh})}}{R_p} \times 100$$

(2)

Here, $R_p$ and $R_{p(\text{inh})}$ is the polarization resistance observed in the absence and presence of PMDH.

Figure 3 is a circuit generally used to describe the aluminium acid interface model (Mansfeld, 1981):

The surface coverage values were calculated from following equation (Abd El Rehim et al., 2004):

$$\theta = \frac{1 - R_p}{R_{p(\text{inh})}}$$

(3)

where $R_p$ and $R_{p(\text{inh})}$ are the polarization resistance without and with inhibitor, respectively.

3.2 Linear polarization

Figure 4 shows the anodic and cathodic polarization curves of pure aluminium in 0.1 M HCl in the absence and presence of various concentrations of PMDH at 298°C. The electrochemical parameters ($i_{corr}$, $E_{corr}$, $b_a$ and $b_c$) associated with polarization measurements and the inhibitor efficiency IE per cent at different inhibitor concentrations are listed in Table II, where $i_{corr}$, $b_a$ and $b_c$ are the corrosion current density, anodic and cathodic Tafel slopes, respectively. It can be observed that $E_{corr}$ shifted to more positive values with the increase in inhibitor concentration and this suggests that the inhibitor influences anodic areas.

For linear polarization, the inhibition efficiency (IE per cent) at different inhibitor concentrations and temperatures were calculated from the equation (Yurt et al., 2006):

$$\text{IE percent} = \frac{i_{corr} - i_{corr(\text{inh})}}{i_{corr}} \times 100$$

(4)

Figure 3 The equivalent circuit model used to fit the experimental results
where, $i_{\text{corr}}$ and $i_{\text{corr(inh)}}$ are the corrosion current densities in the absence and presence of the inhibitor.

The polarization resistance ($R_p$) can be calculated using the Stern-Geary equation:

$$R_p = \frac{b_x \cdot b_z}{2.3(b_x + b_z) i_{\text{corr}}}$$ \hspace{1cm} (5)

### 3.2.1 Effect of temperature

The effect of temperature on the efficiency of the inhibitor in 1 M HCl at temperatures ranging from 25°C to 55°C was obtained to calculate the thermodynamics parameters. The results are given in Table II.

#### 3.3 Adsorption isotherm

For determination of the adsorption process, the values of surface coverage ($\theta$) of different concentrations of PMDH obtained from the polarization measurements in the temperature range (25-55°C) were used.

The metal surface mostly was covered by the adsorbed water molecules. The inhibitor anti-corrosion properties come from the ability to block the charge transfer process on the electrode-electrolyte interphase by replacing the water molecules and ions adsorbed on the electrode surface. This effect can be seen from the decrease of the $C_{dl}$ discussed in Section 3.1:

$$\text{Org}_{(\text{sol})} + n \text{H}_2\text{O}_{(ads)} \rightarrow \text{Org}_{(ads)} + n \text{H}_2\text{O}_{(sol)}$$

$$\text{Org}_{(sol)} + n \text{H}^+_{(ads)} + n\text{Cl}^-_{(ads)} \rightarrow \text{Org}_{(ads)} + n \text{H}^+_{(sol)} + n\text{Cl}^-_{(sol)}$$

where, $n$ indicates the number of molecules that are replaced by the inhibitor molecule, Org$_{(sol)}$ and Org$_{(ads)}$ are the organic molecules in the aqueous solution and adsorbed on the surface of metal, respectively, H$_2$O$_{(ads)}$ and H$_2$O$_{(sol)}$ are water molecules adsorbed on the metal surface and free water molecules in the solution, respectively. $n$H$_{(ads)}$ + nCl$_{(ads)}$ are the ions adsorbed on the metal surface and H$_{(sol)}$ + Cl$_{(sol)}$ are ions in the solutions, respectively.

Several adsorption isotherms were tested for the determination of adsorption behaviour of PMDH on aluminium surface in HCl solution, and the Langmuir adsorption isotherm was chosen and can be given by:

**Table II** Fitting corrosion parameters of aluminium in 1 M HCl on the presence and absence of different concentrations of PMDH obtained from polarization measurements at four temperatures

<table>
<thead>
<tr>
<th>C (M)</th>
<th>T (K)</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$b_x$ (mV/dec)</th>
<th>$b_z$ (mV/dec)</th>
<th>$R_p$ (V cm$^2$)</th>
<th>$i_{\text{corr}}$ (mA cm$^2$)</th>
<th>CR (mm/year)</th>
<th>$\theta$</th>
<th>IE %</th>
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<td>52</td>
<td>1.650</td>
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<td>247</td>
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<td>293</td>
<td>223</td>
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<td>54</td>
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<td>728</td>
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<td>328</td>
<td>-1,200</td>
<td>227</td>
<td>179</td>
<td>368</td>
<td>112</td>
<td>2.939</td>
<td>0.020</td>
<td>2</td>
</tr>
</tbody>
</table>
where:

\[ K_{ads} = \frac{\theta}{C_{inh}(1 - \theta)} \]  \hspace{1cm} (6)

\[ K_{ads} = \exp \left( \frac{-\Delta G_{ads}}{RT} \right) \]  \hspace{1cm} (7)

where:

- \( R \) Universal gas constant.
- \( T \) Temperature.
- \( \Delta G_{ads} \) Free energy of adsorption.

The estimation of the adsorption equilibrium constant \( K_{ads} \) at 25°C for 0.01 M PMDH gives a value of 4,082 dm\(^3\) mol\(^{-1}\), which gave \( \Delta G_{ads} = -20.60 \) kJ mol\(^{-1}\) mol. The negative sign and values of free energy for adsorption of PMDH on the metallic surface (less than \(-40 \) kJ mol\(^{-1}\) mol) for all concentrations of this inhibitor suggest that the adsorption occurs by a spontaneous physical mechanism.

Activation energies for the aluminium dissolution process can be evaluated from the following relationship (Abd El Rehim et al., 2001):

\[ \log \text{ (corrosion rate) } = \log A - \left( \frac{E_a}{2.303RT} \right) \]  \hspace{1cm} (8)

where:

- \( E_a \) Activation energy.
- \( T \) Temperature.

Plotting log (corrosion rate) versus \( 1/T \) gave a straight line with a slope for all temperatures (Figure 8) of \(-E_a/2.303RT\). The activation energies at all temperatures were positive, which shows that the corrosion rate increases with desorption of the inhibitor molecules from the electrode surface. The activation energy also decreases with the inhibitor’s concentrations as in Table III, because large amounts of adsorbed inhibitor needs larger energy for desorption of the inhibitor. This fact also indicates that the adsorption of the inhibitor occurs through physical mechanism (Ashassi-Sorkhabi et al., 2005).

The enthalpy of activation (\( \Delta H^+ \)) and the entropy of activation (\( \Delta S^+ \)) for the corrosion of Al in HCl 1 M in the
**Figure 8** Plotting log corrosion rate vs 1/T to calculate the activation energy of corrosion process in the presence of inhibitor

![Graph showing log corrosion rate vs 1/T](image)

**Table III** Thermodynamic corrosion parameters for aluminium corrosion in absence and presence of various concentrations of PMDH

<table>
<thead>
<tr>
<th>C (M)</th>
<th>E_a (kJ mol⁻¹)</th>
<th>-ΔH° (kJ mol⁻¹)</th>
<th>S° (J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
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<tr>
<td>0.01</td>
<td>12.963</td>
<td>17.92</td>
<td>-168</td>
</tr>
<tr>
<td>0.004</td>
<td>13.355</td>
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<td>-170</td>
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<td>0.001</td>
<td>14.976</td>
<td>14.73</td>
<td>-174</td>
</tr>
<tr>
<td>0.0004</td>
<td>15.964</td>
<td>13.45</td>
<td>-176</td>
</tr>
</tbody>
</table>

absence and presence of different concentrations of PMDH were obtained by applying the transition-state equation (Putilova et al., 1960):

\[
\text{Log} \left( \frac{\text{corrosion rate}}{T} \right) = \text{Log} \left( \frac{R}{hN} \right) + \left( \frac{\Delta S^o}{2.303R} \right) - \frac{\Delta H^o}{2.303RT} \tag{9}
\]

where:
- \( h \) Planck’s constant.
- \( N \) Avogadro’s number.

A plot of log (corrosion rate/T) vs 1/T gives a straight line with slope of \( (\Delta H^o/2.303RT) \) and intercept of \( \log \left( \frac{R}{hN} \right) + \left( \frac{\Delta S^o}{2.303R} \right) \) from these equations \( \Delta H^o \) and \( \Delta S^o \) can be estimated (Figure 9). All thermodynamic results were listed in Table III. The negative values of \( \Delta S^o \) implies that the activated complex in the rate determining step represents an adsorption process and not a desorption process, where the decrease in disordering from the adsorption of the inhibitor molecules to the aluminium surface has taken place.

**3.5 Scanning electron microscope**

Figure 10 shows the aluminium surface after immersion in different concentration of inhibitor. Images show that with increasing PMDH concentration, corrosive surface area decreases.

**4. Discussion**

The impedance plots show that the impedance response of aluminium changed after the introduction of PMDH in 1 M HCl. The results indicate that the impedance response consists of single capacitive semicircles, showing that the corrosion process was mainly charge-transfer controlled (Trabanelli et al., 2005). The high-frequency region of the impedance and phase angle describes the behaviour of an inhomogeneous surface layer, while the low-frequency contribution shows the kinetic response for the charge transfer reaction (Morad, 2000).

By increasing the concentration of inhibitor, the \( C_{dl} \) values tend to decrease and the inhibition efficiency (IE per cent) and polarization resistance (\( R_p \)) increase. The decrease in \( C_{dl} \) is in accordance with the increased adsorption of the PMDH on the aluminium surface which displaces the \( H^+ \) and \( Cl^- \) ions and blocks the charge transfer process across the electrode/electrolyte interface, thus increasing the inhibition efficiency (IE per cent) and polarization resistance (\( R_p \)).

The decrease of \( C_{dl} \) with the increase of PMDH concentration also shows that the adsorption of PMDH molecules at the aluminium surface will increase in the thickness of the electrical double layer and decrease the local dielectric constant (Bentiss et al., 1999). The data obtained from EIS are in agreement with that obtained from potentiodynamic polarization.

The results listed in Table II show that with the increase in inhibitor concentration, the corrosion current density and corrosion rate decrease and polarization resistance increases. With increasing temperature, polarization resistance decreases, corrosion current and, therefore, corrosion rate increases. This can be explained by the desorption of the inhibitor molecules from the aluminium surface and decrease in the strength of adsorption process at higher temperatures. This shows that there is physical adsorption of the inhibitor molecules on the metal surface.
Figure 10 SEM images of aluminium surface before corrosion and after immersion in different concentration of acid

Notes: (a) 1M HCl, (b) 0.01 M, (c) 0.004 M, (d) 0.001 M, and (e) 0.0004 M
5. Conclusion

From the data obtained in this investigation, it can be concluded that benzene-1,2,4,5-tetra carboxylic di anhydride (PMDH) showed good corrosion inhibition properties against aluminium corrosion in the acid media. EIS measurements gave the decrease of $C_{dl}$ with the increase in inhibitor concentrations, which can be explained by increased adsorption of the inhibitor on the aluminium surface, which displaces the adsorbed $H_2O^+$ and $Cl^-$ ions. The inhibition efficiency (IE per cent) decreased with increasing temperature as a result of higher desorption of the inhibitor from the aluminium surface and the efficiency increased when the concentration increased for all temperatures. Adsorption of this inhibitor on the aluminium surface can be closely modelled to the Langmuir isotherm. The negative values of $\Delta G_{ads}$ show that the adsorption is spontaneous and the activation energy decrease with addition of inhibitors. Thermodynamic data suggest physical adsorption for the inhibitor on Al surface. The scanning electron microscope (SEM) images show the retarding of aluminium corrosion in acidic solution by this inhibitor.

References


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