Aminolysis of polyethylene terephthalate waste as corrosion inhibitor for carbon steel in HCl corrosive medium

R. S. Abd El-Hameed

Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt

ABSTRACT

Soft drink bottles was subjected to depolymerization through aminolysis using mono ethanol amine (MEA) in the presence of sodium acetate as a catalyst the product of pol(bis(2-hydroxyethylene)terephthalamide (PHETA) was evaluated as corrosion inhibitors for C-Steel in 1 M HCl by using weight loss, open circuit potential and potentiodynamic polarization measurements, the polarization curves indicate that these compound act as mixed type inhibitors. The inhibition efficiency increase with increasing the concentration of the inhibitors and decreases with increasing the temperature, the values of activation energy($E_a$) and free energy of adsorption ($\Delta G_{ads}$) indicated that the type of adsorption was chemical adsorption. The inhibition occurs through adsorption of the inhibitor molecules on the metal surface without modifying the mechanism of corrosion process. The adsorption of the inhibitor on C-Steel surface was found to follow the Langmuir adsorption isotherm. Scanning electron microscope (SEM) was used to study the surface morphology of steel surface in absence and presence of 200 ppm of the used inhibitor.

Key words: Recycled Plastic Waste, Hydrochloric acid, Corrosion Inhibitors, Carbon Steel and Adsorption isotherm.

INTRODUCTION

In the 1980s, polyethylene terephthalate, (PET) began to be used popularly for the production of disposable soft drink bottles and in 1987, more than 700 million pounds of PET were consumed in their production [1]. As a result of the diversity of its applications in a high volume of consumer products, large amount of PET waste is also generated, which includes polymer manufacturing waste as well as the products after the end of their useful life. (PET) is a worldwide used polymer, and packaging is one of its most important applications. Due to its high resistance to the atmospheric and biological agents, this polymer is not considered as...
biodegradable. PET is not a hazardous product, but its waste quantity increases drastically. With the increasing pressure of keeping the environmental clean. Recycling of PET waste is an ecofriendly manner is the only solution. PET waste can be recycled by different methods like physical recycling and chemical recycling. Chemical recycling is the reaction of PET with various reagents to obtain products that are used in the chemical industry [2], the chemical recycling of PET has been the subject of keen interest as a valuable feedstock for different chemical processes. During chemical recycling, PET waste can be depolymerised to base monomers or oligomers. With the use of solvent of depolymerization, generally called solvolysis of polymer, methanolysis [3-5] and glycolysis [6,7] are the main possible routes. Hydrolysis [8-12] of PET is also possible using water under pressure. Aminolysis is another method of chemical degradation of PET, which has been little explored as compared to other techniques.

Carbon steel is widely used as the constructional material in most of the major industries particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. The major problem of Carbon steel is its dissolution in acidic medium. Corrosion of iron and steel in acidic aqueous solutions is one of the major areas of concern in many industries where in acids are widely used for applications such as acid pickling, acid cleaning, acid descaling, and oil well acidizing. Because of general aggressiveness of acid solution the materials of construction are getting corroded easily.

Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching of metals, acidization of oil wells and in cleaning of scales because it is more economical, efficient and trouble-free, compared to other mineral acids [13, 14]. It is very important to add corrosion inhibitors to prevent metal dissolution and minimize acid consumption [15-17]. Most well known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. The inhibiting action exercised by organic compounds on the dissolution of metallic species is normally related to interactions by adsorption between the inhibitors and the metal surface. This process is considered as interface inhibition, according to Fischer’s classification [18, 19]. The surfactant inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and easy production [20-25]. The adsorption of the surfactant on the metal surface can markedly change the corrosion resisting property of the metal [26, 27], and so the study of the relationship between the adsorption and corrosion inhibition is of great importance.

In the previous works [28-31], glycolysis of PET waste with diethanol amine (DEA)and triethanol amine (TEA) and their modified products and oligomeric surfactants was used as a cheap and save corrosion inhibitors for steel in aqueous medium.

The present work is the one from a series aimed to alleviate of environmental pollution by converting PET waste into useful products, and to evaluation the inhibition action of plastic waste on the corrosion of some metals and alloys, in different aqueous medium.

In the present work, mono ethanol amine (MEA) was used to convert PET waste into water soluble amide and evaluation of the prepared materials as corrosion inhibitors for C- Steel in 1M HCl at different temperatures.
MATERIALS AND METHODS

Materials
Poly(ethylene terephthalate) (PET) waste is collected from beverage bottles. Monoethanol amine (MEA) and sodium acetate were obtained from Aldrich Chemical Co., England. The aggressive solution (1 M HCl) was prepared by appropriate dilution of analytical grade 36% HCl with double distilled water.

Recycling Process
The reaction of PET with diethanolamine (DEA) and triethanolamine was discussed in the previous articles [29] in the present work PET waste was depolymerized with monoethanolamine (MEA), at weight ratio of PET to monoethanolamine (MEA) 1:1 (wt% of PET: wt% of MEA) using 1.0% of sodium acetate as catalyst (by weight based on weight of PET). The reaction mixtures were heated under vigorous stirring in nitrogen atmosphere at temperature about 170–190 °C for 4 h and at 200 °C for 3 h. The temperature of the reaction was then lowered to 100 °C for 1 h. The mixture was allowed to cool to room temperature. At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out of the product, poly(bis(2-hydroxy ethylene) terephthal) amide (PHETA). White crystalline powder of (BHETA) was obtained by recrystallisation in distilled water, the chemical structure of (PHETA) was confirmed from their IR spectra. The presence of strong band at 1053 and 3289 cm⁻¹ indicating the presence of primary alcohol (-CH₂-OH).[32] The peaks for secondary amide stretching are observed at 1314, 1553 and 3368 cm⁻¹, and the band observed at 810 cm⁻¹ for (PHETA) is assigned to –CH₂ out– of – plane bending of p-substituted phenyl. This confirms the presence of phenyl rings in depolymerized product (PHETA). Which have the following chemical structure Figure (1).

Weight loss measurements
Carbon steel alloy with the dimensions of 2x2x0.05 (cm) with chemical composition (wt %) of 0.29 C, 1.25 Mn, 0.03 P, 0.03 Sn, 0.04 Cr, 0.04 Mo, and 0.027 Si and the remainder iron. The samples were polished successively with fine grade emery papers, cleaned with acetone, washed with double distilled water, dried, weighed and then introduce into test solution. Weight loss measurements were carried out in a double wall glass cell equipped with a thermostat-cooling condenser.
Potentiodynamic polarization measurements
The working electrode was made from mild steel rod that has the same composition as mentioned in point 2.2. The rod was axially embedded in araldite holder to offer an active flat disc shaped surface of an area 1 cm$^{-2}$. Prior to each experiment, the working electrode was polished successively with fine emery paper, rinsed with acetone, washed with double distilled water and finally dried before dipping into the electrolytic cell. A platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode to which all potentials are referred.

The electrochemical experiments are performed using radiometer analytical, Volta master (PGZ301, DYNAMIC ELS VOLTAMMETRY). The experiments were carried out by changing the electrode potential automatically from the starting potential towards more positive values at the required scan rate till the end of the experiments.

Open circuit potential
The potential of steel electrode was measured against saturated calomel electrode (SCE) in 1 M HCl solution in absence and presence of 200 ppm of the used inhibitors at 25 °C. All measurements were carried out using Multi-tester until the steady-state potentials are reached.

Scanning electron microscopy (SEM)
The surface of the carbon steel was analyzed after the corrosion tests, by an Olympus PME3 optical microscope. The energy of the acceleration beam employed was 20 kV. All micrographs were carried out at a magnification power of X = 500.

RESULTS AND DISCUSSION
The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [28]. The choice of the inhibitor is based on two considerations:

First: it could be synthesized conveniently from relatively cheap raw materials,

Secondly: it contains the electron cloud on the aromatic ring or the electronegative atoms such as N$_2$ and O$_2$ in the relatively long chain compounds [30]. In this respect, the present corrosion inhibitors were prepared from recycled PET waste and introducing MEA in their chemical structure to increase their abilities to dissolve in water and to use as corrosion inhibitors for C-steel. The corrosion of C-steel in 1 M HCl solution at different temperatures was studied by open circuit potential, potentiodynamic polarization techniques and weight loss measurements.

Open circuit potential measurements
The potential of carbon steel electrodes immersed in 1M HCl solution was measured as a function of immersion time in the absence and presence of 200ppm of (PHETA) as shown in Figure(2). It is clear that the potential of carbon steel electrode immersed in 1M HCl solution (blank curve) tends towards more negative potential firstly, giving rise to short step. This behavior was reported by West [33], which represents the breakdown of the pre-immersion air formed oxide film presents on the surface according to the following equation:
This is followed by the growth of a new oxide film inside the solution, so that the potential was shifted again to more noble direction until steady state potential is established. Addition of the inhibitor molecules to the aggressive medium shift the potential to more positive direction (less negative) and as the concentration of the inhibitor increases, the corrosion potential was shifted to more noble direction.

![Potential–time curves for carbon steel immersed in 1M HCl solution in the absence and presence of different concentrations of (PHETA).](image)

Addition of the inhibitor molecules shift the potential to more positive direction (less negative) and as the concentration of the inhibitor increases, the corrosion potential was shifted to more noble direction.

In all curves the steady-state values are always more negative than the immersion potential suggesting that before the steady state condition is achieved the steel oxide film has to dissolve.

**Potentiodynamic polarization measurements**

Figures 3 show the Tafel polarization curves measured on C-steel electrodes in 1M HCl solutions at 25°C in the absence and presence of PHETA inhibitor concentrations. The figure clearly indicate that the presence of inhibitor causes a marked decrease in the corrosion rate, i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to adsorption of inhibitor over the corroded surface [34]. The values of corrosion current densities ($I_{corr}$), corrosion potential ($E_{corr}$), the cathodic Tafel slope ($\beta_c$), anodic Tafel slope ($\beta_a$), and the inhibition efficiency ($IE$) as functions of (PHETA) concentration, were calculated from the curves of Figs.3 using Voltamaster 4 corrosion software.
and given in Table 1. In the mean time the corrosion current decreases substantially, so the inhibition efficiency increases

(Table 1), where the \( IE\% \) was calculated from the relation:

\[
IE \% = \left( \frac{I_{c, \text{un}} - I_{c, \text{inh}}}{I_{c, \text{un}}} \right) \times 100
\]

Where \( I_{c, \text{un}} \) is the corrosion current in the absence of inhibitor; \( I_{c, \text{inh}} \) the corrosion current in the presence of inhibitor. Table 1 reveals that the corrosion current decreases obviously and \( IE\% \) increases with the inhibitor concentration. The presence of PHETA does not remarkably shift the corrosion potential, while the anodic and cathodic Tafel slopes slightly changed upon addition of increasing inhibitor concentration. Therefore, PHETA can be classified as mixed – type inhibitor in HCl. The same results have been reported with other organic inhibitors in acidic medium [29, 30, 35]. Both anodic and cathodic reactions of electrode are drastically inhibited, probably being caused by a strong adsorption layer which covers both anodic and cathodic reactive sites on the C-steel surface. The slight change in the anodic and cathodic Tafel slopes suggests that the inhibitor molecules affect the corrosion rate of carbon steel without changing the metal dissolution mechanism [36].

Fig.3. Tafel polarization curve for C-steel in 1M HCl at 25\(^\circ\)C in absence and presence of different concentrations of PHETA.
Table 1: variation of polarization parameters for carbon steel in 1M concentration of HCl at 25°C with different concentrations of PHETA inhibitor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc., ppm</th>
<th>$I_{corr}$, mA/cm$^2$</th>
<th>$E_{corr}$, mV</th>
<th>Rp, ohm.cm$^2$</th>
<th>$b_a$, mV/decade</th>
<th>$b_c$, mV/decade</th>
<th>C.R. (MPY)</th>
<th>IE%</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>425.80</td>
<td>101.1</td>
<td>11.2</td>
<td>118.2</td>
<td>343</td>
<td>4980</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PHETA</td>
<td>50</td>
<td>39.46</td>
<td>179.8</td>
<td>143</td>
<td>331</td>
<td>347</td>
<td>461.5</td>
<td>90.7</td>
<td>0.907</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>25.79</td>
<td>172.4</td>
<td>205</td>
<td>309</td>
<td>319</td>
<td>301.6</td>
<td>93.9</td>
<td>0.939</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>25.14</td>
<td>164.9</td>
<td>232</td>
<td>297.7</td>
<td>349</td>
<td>294.1</td>
<td>94.1</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>22.73</td>
<td>168.6</td>
<td>235</td>
<td>311.8</td>
<td>342</td>
<td>265.9</td>
<td>94.7</td>
<td>0.947</td>
</tr>
</tbody>
</table>

Weight loss measurements
Effect of inhibitor concentration
Weight loss (mg/ cm$^2$) of the surface area was determined in an open system at various time intervals. Weight loss of the steel sample versus time of immersion was plotted in Figure (4). It is evident from these figures that in all cases. The weight loss increases with increasing of the time of immersion. The curves obtained in the presence of additives fall significantly below that of free acid in all cases. In this respect, the increase of the additive concentration was accompanied by a decrease of weight loss and an increase of the percentage of inhibition [29].

![FIG 4. Weight loss-time curves of C-steel in 1 M HCl in absence and presence of different concentration of inhibitor PHETA at 303 K.](image-url)
The corrosion inhibition efficiency (%IE) was calculated by the following equation:

\[
%\text{IE} = \left(\frac{\Delta w - \Delta w_i}{\Delta w}\right) \times 100
\]  

(3)

Where \( \Delta w \) and \( \Delta w_i \) are the weight loss per unit area in absence and presence of the inhibitor respectively. \( \Delta w \) can be calculated from the following equation:

\[
\Delta w = w_b - w_a
\]  

(4)

Where \( w_b \) and \( w_a \) are the weight of the specimen before and after reaction, respectively. The obtained data of (%IE) and rate of corrosion (C.R.) of PHETA were summarized and listed in Table (2). The data show that C.R. value was decreased with increase of inhibitors concentration. On the other hand, the inhibition efficiency was increased with increasing of inhibitors concentration. So that the inhibitors compounds may be chemically adsorbed on the steel surface and cover some sites of the electrode surface. The chemical adsorption can be explained on the basis of the effect of chemical structure of inhibitors on its inhibition efficiency. In this respect, the benzene ring and the carbonyl group (C=O) PHETA can form a big (\( \pi \)) bond accordingly, not only the (\( \pi \)) of benzene and carbonyl enter unoccupied orbital of iron, but also, the \( \pi^* \) orbital can accept the electron of d orbital of iron to form feed back bonds, which produce more than one center of chemical adsorption on the steel surfaces [31].

<table>
<thead>
<tr>
<th>conc.ppm</th>
<th>Wt. loss mg.cm²</th>
<th>Corrosion rate (C.R.), mg.cm⁻² day⁻¹</th>
<th>( \theta )</th>
<th>%IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>65</td>
<td>105.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>7.3</td>
<td>11.8</td>
<td>0.89</td>
<td>89</td>
</tr>
<tr>
<td>100</td>
<td>6.4</td>
<td>10.3</td>
<td>0.90</td>
<td>90</td>
</tr>
<tr>
<td>150</td>
<td>5.7</td>
<td>9.2</td>
<td>0.91</td>
<td>91</td>
</tr>
<tr>
<td>200</td>
<td>4.2</td>
<td>6.8</td>
<td>0.935</td>
<td>93.5</td>
</tr>
</tbody>
</table>

**Effect of temperature**

To elucidate the mechanism of inhibition and to determine the kinetic parameters of the corrosion process weight loss measurements were performed at 303,313,323,333K. The effect of temperature on the corrosion inhibition efficiency of C- steel in the presence of the inhibitor is graphically represented in Figure (5).

The inhibition efficiency decreased with increase in temperature, leading to the conclusion that the protective film of these compounds formed on the carbon steel surface is less stable at higher temperature; which may be due to the desorption of some adsorbed molecules from the surface of the carbon steel at higher temperature due to which greater area of the metal is exposed to the acidic environment. The apparent activation energy (\( E_a \)) of metal corrosion in acid media can be calculated from the Arrhenius equation [40]:

\[
\log (C.R.) = \left(\frac{E_a}{RT}\right) + A
\]  

(5)
where $E_a$ is the apparent activation energy for the corrosion of carbon steel, $R$ is the universal gas constant, $A$ is Arrhenius pre exponential factor and $T$ is the absolute temperature. Figure(6) depicts the plot of $\log C.R.$ vs. $1/T$ and the values of $E_a$ obtained from the slope of the plot are given in Table(3).

![Graph](image)

**Fig. 5.** Effect of temperature on I.E for C-Steel in 1M HCl in the presence of different concentrations of the inhibitor PHETA.

<table>
<thead>
<tr>
<th>Inhibitor concentration (ppm)</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
<th>$\Delta H_a$ (kJmol$^{-1}$)</th>
<th>$\Delta S_a$ (Jmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>44</td>
<td>41.22</td>
<td>-154</td>
</tr>
<tr>
<td>50</td>
<td>53</td>
<td>50.4</td>
<td>-145</td>
</tr>
<tr>
<td>100</td>
<td>56.4</td>
<td>54</td>
<td>-143</td>
</tr>
<tr>
<td>150</td>
<td>68.96</td>
<td>58.8</td>
<td>-137</td>
</tr>
<tr>
<td>200</td>
<td>61.56</td>
<td>62</td>
<td>-125</td>
</tr>
</tbody>
</table>

Table 3. Values of activation parameters for C-Steel in 1M HCl in the absence and presence of different concentrations of the inhibitor PHETA

The higher value of activation energy ($E_a$) in the presence of inhibitor than in its absence is attributed to its physical adsorption, its chemisorption is pronounced in the opposite case [37, 38].
In the present study the higher value of $E_a$ for carbon steel in presence of PHETA derived from plastic waste compared to that in its absence is attributed to its physical adsorption. Szauer and Brand [39] explained that the increase in $E_a$ can be attributed to an appreciable decrease in the adsorption of the inhibitor on the steel surface with increase in temperature and a corresponding increase in corrosion rates occurs due to the fact that greater area of metal is exposed to acid environment. An alternative form of Arrhenius equation is the transition state equation [40]:

$$C.R. = \left( \frac{RT}{Nh} \right) \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( - \frac{\Delta H_a}{RT} \right) \quad (6)$$

where, $h$ is the Plank’s constant, $N$ is the Avogadro’s number, $\Delta S_a$ is the entropy of activation, and $\Delta H_a$ is the enthalpy of activation. A plot of log (C.R./T) vs. 1/T gave a straight line as shown in Figure(7) with a slope of (-\(\Delta H /2.303R\)) and an intercept of [log(R/Nh) + (\(\Delta S /R\))], from which the values of $\Delta H_a$ and $\Delta S_a$ were calculated and listed in Table 3.
The positive values of $\Delta H_a$ for corrosion of carbon steel in the presence and absence of the inhibitor reflect the endothermic nature of metal dissolution process. The increase in $\Delta H_a$ with increase in the concentration of the inhibitor for steel corrosion reveals that decrease in carbon steel corrosion rate is mainly controlled by kinetic parameters of activation [39].

The entropy of activation values are less negative for inhibited solutions than that for the uninhibited solutions. This suggests that an increase in randomness occurred while moving from reactants to the activated complex [41].

**Thermodynamic parameters of dsorption**

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the metal surface has to be known. The degree of surface coverage ($\Theta$) for different concentration of the inhibitor ($C_{inh}$) has been evaluated. The data were tested graphically by fitting to various isotherms. A straight line with correlation coefficient nearly equal to 1.0 was obtained on plotting $C_{inh}/\Theta$ against $C_{inh}$ as shown in Figure(8) suggesting,

Adsorption of the compound on the carbon steel surface followed Langmuir adsorption isotherm model. It is interpreted from the graph that, adsorption of the inhibitor on the carbon steel surface followed Langmuir adsorption isotherm at all studied temperatures.
According to this isotherm, the surface coverage ($\theta$) is related to inhibitor concentration $C_{\text{inhi}}$ by equation

$$\frac{C_{\text{inhi}}}{\theta} = \frac{1}{K_{\text{ads}}} + C$$

(7)

where, $K_{\text{ads}}$ is equilibrium constant of the equilibrium adsorption process. This isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species.

The $K_{\text{ads}}$ values can be calculated from the intercept lines on the $C_{\text{inhi}}/\theta$ axis. This is related to the standard free energy of adsorption ($\Delta G_{\text{ads}}$) by equation:

$$\Delta G_{\text{ads}} = -RT \ln(55.5 K_{\text{ads}})$$

(8)

where, $R$ is the gas constant and $T$ is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/L. The values of $\Delta G_{\text{ads}}$ for the inhibitor on the surface of carbon steel are given in Table 4.

The negative value of $\Delta G_{\text{ads}}$ indicated spontaneous adsorption of the inhibitor on the mild steel surface. Generally, the magnitude of $\Delta G_{\text{ads}}$ around -20kJ/mol or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption). Those around -40kJ/mol or more negative are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions). In the present work, the calculated values $\Delta G_{\text{ads}}$ at 303K for mild steel is -39.6 kJ/mol, which indicate that adsorption of the inhibitor on the mild steel surface involves both
physical and chemical process[43-46]. But the inhibition efficiency decreased with increasing temperature indicating inhibitor adsorbed predominantly physically on the surface of steel. The enthalpy of adsorption ($\Delta H_{ads}$) can be calculated from the rearranged Gibbs-Helmholtz equation:

$$\frac{\Delta G_{ads}}{T} = \left( \frac{\Delta H_{ads}}{T} \right) + K$$  \hspace{1cm} (9)

The variation of $\Delta G_{ads}/T$ with $1/T$ gave a straight line with a slope of $\Delta H_{ads}$ as shown in Figure(9). The entropy of adsorption $\Delta S_{ads}$ was calculated using the following thermodynamic equation:

$$\Delta S_{ads} = \frac{(\Delta H_{ads} - \Delta G_{ads})}{T}$$  \hspace{1cm} (10)

The calculated values of heat of adsorption and entropy of adsorption are listed in Table 4.

![Figure 9](image_url)

**Figure 9.** Relation between ($\Delta G_{ads}/T$) and $1/T$ for C-Steel in 1M HCl solution.

**Table 4.** Values of thermodynamic parameters for the adsorption of the inhibitor in 1M HCl on the C-Steel at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>K (mol$^{-1}$)</th>
<th>$\Delta G_{ads}$ (kJmol$^{-1}$)</th>
<th>$\Delta H_{ads}$ (kJmol$^{-1}$)</th>
<th>$\Delta S_{ads}$ (Jmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>61006</td>
<td>-139.6</td>
<td>-10.89</td>
<td>98.08</td>
</tr>
<tr>
<td>313</td>
<td>51801</td>
<td>-140.7</td>
<td>-10.89</td>
<td>97.76</td>
</tr>
<tr>
<td>323</td>
<td>47290</td>
<td>-142.5</td>
<td>-10.89</td>
<td>98.03</td>
</tr>
<tr>
<td>333</td>
<td>42123</td>
<td>-143.4</td>
<td>-10.89</td>
<td>98.01</td>
</tr>
</tbody>
</table>
It is well known fact that adsorption is an exothermic phenomenon accompanied by a decrease in entropy [47]. In aqueous solutions the adsorption of the organic molecule is generally accompanied by desorption of water molecules [48].

\[
\text{Inhibitor} \text{ (sol)} + x \text{H}_2\text{O} \text{ (ads)} \rightleftharpoons \text{Inhibitor} \text{ (ads)} + x \text{H}_2\text{O} \text{ (sol)} \quad (11)
\]

The negative sign of \(\Delta H_{\text{ads}}\) indicated the exothermic process of adsorption of the inhibitor on carbon steel surface in HCl. The positive value of \(\Delta S_{\text{ads}}\) in the presence of inhibitor can be attributed to the increase in the solvent entropy and more positive desorption entropy. It is also interpreted that the increase of disorderness is due to more water molecules which can be desorbed from the metal surface by one inhibitor molecule. Therefore it is revealed that decrease in the enthalpy is the driving force for the adsorption of the inhibitor on the surface of carbon steel [49-50].

**Mechanism of Corrosion Inhibition**

In hydrochloric acid medium, the metal surface is negatively charged due to the specifically adsorbed chloride ions on the metal surface.

\[
\text{Fe} + \text{Cl}^- \longrightarrow (\text{FeCl}^-)_{\text{ads}} \quad (12)
\]

In acidic solution, the oxygen and nitrogen atoms of the PHETA of the inhibitor can be protonated easily, due to high electron density on it, leading to positively charged inhibitor species. The adsorption can occur via electrostatic interaction between positively charged inhibitor molecule and negatively charged metal surface[ 51,52] leading to physisorption of the inhibitor molecules. Further, co-ordinate bond may be formed between unshared e- pairs of unprotonated nitrogen atom of the inhibitor and vacant d-orbitals of metal surface atoms. Additionally inhibitor molecule may be chemically adsorbed due to interaction of \(\pi\) electrons of the benzene ring of the inhibitor with vacant d-orbitals of metal [ 44].

**Surface Studies by Scanning Electron Microscopy**

In order to evaluate the conditions of the metal surface in contact with acid solution in the absence and presence of inhibitor, a surface analysis was carried out, using scanning electron microscope, immediately after the corrosion tests. The carbon steel samples in 1M HCl solution with and without optimal concentration of the inhibitor were subjected to analysis. SEM images shown in Figure(10) shows, surface corrosion of carbon steel decreased remarkably in the presence of the inhibitor. Inspections of the figures reveal that there is severe damage, clear pits and cavities on the surface of carbon steel in the absence of inhibitor than in its presence. This confirms that metal surface is fully covered with adsorbed inhibitor molecules.
Fig. 10. (A) Optical micrographs of surface of carbon steel after immersion for 10 hours at 30°C in 1M HCl.

Fig. 10. (B) Optical micrographs of surface of carbon steel after immersion for 10 hours at 30°C in 1M HCl+200ppm inhibitor.
CONCLUSION

1) Results obtained from the experimental data show that PHETA derived from plastic waste is a good inhibitor for the corrosion of carbon steel in 1M HCl and inhibition efficiency was more pronounced with increase in the inhibitor concentration.

2) The inhibition efficiency decreased with increase in temperature, leading to the conclusion that the protective film of these compounds formed on the carbon steel surface is less stable at higher temperature.

3) The values of $\Delta G_{ads}$ indicate adsorption of the inhibitor by both physical and chemical process while the decrease in inhibition efficiency with increase in temperature indicated predominate physisorption of the inhibitor.

4) The potentiodynamic polarisation curves imply that, PHETA derived from plastic waste acts as a mixed type inhibitor, for corrosion of carbon steel in 1M HCl.


6) The polarization resistance ($R_p$) value increased with increase in the concentration of the inhibitor.

7) Results obtained from polarization and weight loss measurements are in good agreement with each other.

REFERENCES