Performance Evaluation of Polypropylene glycol as Corrosion Inhibitor for X60 Pipeline Steel in 15% HCl Solution

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Summary

The toxic nature of most organic and inorganic corrosion inhibitors has necessitated the search for corrosion inhibitors with an excellent environmental profile. The present work is focused on the utilization of polypropylene glycol (PPG) for metallic corrosion control and reports on the corrosion inhibition effect of polypropylene glycol for typical X60 pipeline steel in 15% HCl solution using weight loss, electrochemical impedance spectroscopy, linear polarization resistance and potentiodynamic polarization techniques. Water contact angle measurements and scanning electron microscopy (SEM) were employed for surface morphology characterization. Results obtained show that polypropylene glycol acts as a good corrosion inhibitor for X60 steel in the strong acid environment. Inhibition efficiency increased with increase in PPG concentration. Immersion time and temperature were found to have profound effect on the corrosion inhibition performance of PPG. The potentiodynamic polarization studies revealed that PPG functions as a mixed-type inhibitor. The effective corrosion inhibition potential of PPG could be related to the adsorption of PPG molecules at the metal/solution interface which was found to accord with Langmuir adsorption isotherm model and a protective film formation.

1. Introduction

Acidization of a petroleum oil well is one of the stimulation techniques to enhance oil production. It is carried out by forcing acid solutions through carbon steel tubing into the well to open up near bore channels in the formation and to increase the flow of oil. Several acid-based stimulations fluids are used in the acidization process and are classified into mineral acid (HCl), organic acids (formic and acetic), mixed acids (HCl-formic, HCl-acetic) and retarded acids (gelled, emulsified etc) [1, 2]. HCl is the most commonly used acids in well stimulation treatment because of its reasonable cost, soluble reaction products and its high dissolving power. For matrix stimulation and acid fracturing, 15 – 28% HCl is commonly used. The major problem in using HCl is its high corrosion and fast reaction rate.

In order to reduce the aggressive attack of the tubing and casing materials made of carbon steel, corrosion inhibitors must be added to the acid during the acidization process. Among the several corrosion protection strategies, the use of corrosion inhibitors is cost effective and practical means of controlling corrosion especially in acid environments. Corrosion inhibitors work by adsorbing themselves on the metal surface

forming protecting films thereby isolating the metal from the aggressive ions present in solution.

Some researchers have reported the effectiveness of organic compounds in inhibiting the corrosion of carbon steel in 15% HCl solution [3-5]. Survey of available literature has shown that polymers both synthetic and naturally occurring have been reported as corrosion inhibitors for steel in different corrosive environments [6-9]. Interest in polymers as corrosion inhibitors arise because of their low prices, availability, safe in handling, environmental friendliness, and presence of multiple adsorption centres [10]. However, there is scanty report on the use of polymers as corrosion inhibitor for steel in stimulation acid based fluid such as 15% HCl solution. To the best our knowledge the only available report is on xanthan gum and its graft co-polymer as corrosion inhibitor for mild steel in 15% HCl by Biswas et al. [11]. In our continuous quest to explore polymers as corrosion inhibitors in new and challenging corrosive environments, the present work reports on the corrosion inhibition effect of polypropylene glycol in 15% HCl solution using weight loss and electrochemical methods complemented with surface analysis approach.

2. Experimental

2.1 Materials and materials preparation

The specimens for weight loss and working electrodes from electrochemical experiments were cut into coupons of dimensions 3 x 3 x 0.25 cm from X60 pipeline steel strips with the composition (in wt %) as previously reported [9]. The coupons were ground with a series of emery paper of different grits from # 120 to 800, cleaned in ethanol in ultrasonic bath for 5 minutes to remove impurities, rinsed first with distilled water and followed by acetone and dried in a stream of warm air. The dried specimens were stored in desiccators before use in corrosion studies.

All tests were carried out in 15% HCl prepared by dilution of 36% analytical grade HCl (Eurostar Scientific Ltd, UK) with doubled distilled water. Polypropylene glycol (Sigma-Aldrich); number average molecular, $M_n = 2000 \text{ g mol}^{-1}$ was used as the test inhibitor in the concentration range of 50 – 1000 ppm.

2.2 Weight loss tests

Pre-cleaned and pre-weighed X60 steel samples of uniform size were freely suspended in 250 ml test solutions without and with different concentrations of PPG for 24 h. After this immersion time, the samples were withdrawn and cleaned as previously reported [9]. The difference in weight of the coupons between pre and post immersions was taken as the weight loss. In order to evaluate the effect of temperature on the corrosion inhibition efficacy of PPG, the weight loss experiments were performed at different temperatures in the range 25 to 60 °C.

From the weight loss value, corrosion rate and inhibition efficiency were computed using equations (1) and (2) respectively:

$$ C_R = \frac{W_0 - W_i}{At} $$

(1)
\[ IE\% = \frac{W_o - W_1}{W_o} \times 100 \]  

(2)

where \( W_o \) and \( W_1 \) are the weight losses (g) of X60 steel in the absence and presence of inhibitor (PPG) respectively, \( A \) is the surface area of X60 sample (cm\(^2\)), \( t \) is the immersion time (h), \( C_R \) is the corrosion rate and \( IE \) is the inhibition efficiency.

### 2.3 Electrochemical measurements

Electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) and potentiodynamic polarization (PDP) techniques were used to evaluate the efficacy of PPG as corrosion inhibitor for X60 steel in 15% HCl using Gamry Instrument Potentiostat/ Galvanostat/ZRA (Reference 3000) with a Gamry framework system based on ESA410. Gamry applications include software DC105 for corrosion, EIS300 for electrochemical impedance spectroscopy (EIS), measurements and Echem Analyst 6.0 software package for data fitting. Three electrode systems consisting of X60 steel as working electrode with exposed surface area of 0.7855 cm\(^2\), saturated calomel electrode (SCE) as the reference electrode and graphite rod as the counter electrode. All potentials were measured versus SCE reference electrode. Prior to all electrochemical measurements, the working electrode was immersed in the different test solutions for 1 h which was adequate for a stable E\(_{OCP}\) to be attained. EIS measurements were carried out under potentiostatic conditions in a frequency range from 100 kHz to 100 mHz, with amplitude of 10 mV peak-to-peak, using AC signal at E\(_{OCP}\). LPR experiment was performed from −10 to +10 mV versus E\(_{OCP}\) at the scan rate of 0.125 mVs\(^{-1}\). Polarization curves were recorded at a constant sweep rate of 0.5 mVs\(^{-1}\) from the cathodic potential of −0.30 V to anodic potential of +0.30 V with respect to E\(_{OCP}\).

### 2.4 Surface analysis.

X60 steel coupons of 3 cm × 3 cm dimension prepared as earlier described were immersed in 15% HCl solution without and with the highest concentration (1000 ppm) of PPG for 24 h at 25 °C. The treated steel samples were rinsed with distilled water and dried in a stream of warm air for subsequent surface analysis. The morphology and composition of the corroded steel surfaces immersed in the corrosive medium in absence and presence of PPG were determined using a JEOL JSM 6610- LV scanning electron microscope (SEM). The wetting properties of the surfaces of corroded steel specimens in 15% HCl solution without and with PPG were evaluated by water contact angle measurements using Attension Contact Angle Meter (Biolin Scientific Instrument) by static sessile drop method.
3. Results and discussion

3.1 Potentiodynamic and linear polarization measurements

The potentiodynamic polarization curves for X60 steel in 15% HCl solution without and with different concentrations of PPG are shown in Fig. 1. The electrochemical parameters including corrosion current density ($i_{\text{corr}}$), corrosion potential ($E_{\text{corr}}$), anodic Tafel slope ($\beta_a$), cathodic Tafel slope ($\beta_c$) and inhibition efficiency (IE %) are listed in Table 1.

![Potentiodynamic polarization curves](image)

**Figure 1:** Potentiodynamic polarization curves for X60 steel in 15% HCl in the absence and presence of different concentrations PPG at 25 °C

From the polarization curves shown in Fig.1, it is clear that introduction of PPG into the corrosive medium significantly decreased both the anodic and cathodic current density compared to the blank solution. Inspection of Table 1 revealed that the corrosion potential for the blank solution is $-424$ mV vs SCE with the corresponding corrosion current density of $892 \ \mu$A cm$^{-2}$. In the presence of PPG, the $E_{\text{corr}}$ value is shifted to more anodic side and a significant concentration dependent reduction in corrosion current density is observed. For instance in the presence of 50 and 1000 ppm PPG, the $E_{\text{corr}}$ values of $-401$ and $389$ mV vs SCE and a corresponding $i_{\text{corr}}$ values of 108 and $43.9 \ \mu$A cm$^{-2}$ were obtained. A shift in both the anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel constants in the presence of PPG in comparison to the blank was also recorded. However, only slight changes in both Tafel constants were noticed as PPG concentration changes. This observation as well as the decrease in both anodic and cathodic current density in the presence of PPG clearly indicates that PPG impacted both cathodic and anodic reactions of the corrosion process hence functions as a mixed-type corrosion inhibitor. The inhibition efficiency from the potentiodynamic polarization method was computed using the following expression:

$$IE(\%) = \left(1 - \frac{i_{\text{corr}}}{i_{\text{corr}0}}\right) \times 100$$  \hspace{1cm} (3)
where \( i_{corr} \) and \( \rho_{corr} \) are the corrosion current densities in the absence and presence of inhibitor respectively. The values are listed in Table 1 for the different concentrations of PPG investigated. It is clear from the table that inhibition efficiency increased with increase in PPG concentration reaching the value of 94.7% at the highest concentration (1000 ppm) studied.

**Table 1:** Potentiodynamic polarization (PDP) and Linear polarization resistance (LPR) parameters for X60 steel in 15% HCl without and with PPG at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>( E_{corr} ) (mV/SCE)</th>
<th>( I_{corr} ) (µA cm(^{-2}))</th>
<th>( \beta_a ) (mV dec(^{-1}))</th>
<th>( \beta_c ) (mV dec(^{-1}))</th>
<th>IE (%)</th>
<th>( R_p ) (Ω cm(^2))</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>–424</td>
<td>829.0</td>
<td>101.6</td>
<td>120.2</td>
<td>–</td>
<td>35.8</td>
<td>–</td>
</tr>
<tr>
<td>50</td>
<td>–401</td>
<td>108.0</td>
<td>71.8</td>
<td>81.6</td>
<td>86.9</td>
<td>192.3</td>
<td>81.4</td>
</tr>
<tr>
<td>100</td>
<td>–395</td>
<td>99.5</td>
<td>81.0</td>
<td>104.3</td>
<td>87.9</td>
<td>215.7</td>
<td>83.4</td>
</tr>
<tr>
<td>200</td>
<td>–391</td>
<td>65.8</td>
<td>80.5</td>
<td>102.9</td>
<td>92.1</td>
<td>307.2</td>
<td>88.3</td>
</tr>
<tr>
<td>500</td>
<td>–391</td>
<td>54.1</td>
<td>83.6</td>
<td>111.3</td>
<td>93.5</td>
<td>420.8</td>
<td>91.5</td>
</tr>
<tr>
<td>1000</td>
<td>–389</td>
<td>43.9</td>
<td>78.9</td>
<td>106.8</td>
<td>94.7</td>
<td>425.0</td>
<td>91.6</td>
</tr>
</tbody>
</table>

Linear polarization resistance (LPR) method was also employed to evaluate the corrosion inhibition efficacy of PPG for X60 steel in 15% HCl solution. The polarization resistance \( (R_p) \) and inhibition efficiency \( (IE \%) \) values derived from this technique in the absence and presence of different concentrations of PPG are also given in Table 1. The inhibition efficiency of PPG was calculated from the following equation:

\[
IE(\%) = \left(1 - \frac{R_p^0}{R_p}\right) \times 100
\]

where \( R_p^0 \) and \( R_p \) are the polarization resistance values in the absence and presence of the inhibitor respectively. Data in Table 1 show that polarization resistance increased in the presence of PPG compared to its absence confirming that PPG acts as a good inhibitor for X60 steel corrosion in the strong corrosive medium. The polarization resistance is also observed to increase with increase in PPG concentration. The maximum polarization resistance value of 425 Ω cm\(^2\) was obtained at the optimum PPG concentration (1000 ppm) studied. This polarization resistance corresponds to the inhibition efficiency of 91.6%. The results obtained from the potentiodynamic polarization and linear polarization resistance techniques are in a reasonable good agreement.

### 3.2 Electrochemical impedance spectroscopy measurements

The impedance data recorded on X60 steel immersed in 15% HCl solution without and with different concentrations of PPG are shown in Fig. 2 in (a) Nyquist, (b) Bode modulus and representations. Inspection of the plots revealed that the shape of
Nyquist plots in the absence and presence of inhibitor are similar which indicates an unchanged mechanism of corrosion. The Nyquist plots instead of ideal semicircles are found to be depressed with centre below the real axis. This kind of behavior is often associated with dispersion effect [12]. The depressed nature of semicircles is typical of solid electrodes and is usually attributed to the distribution of active sites, adsorption of inhibitor molecules as well as the formation of porous layers [12, 13]. It is also attributed to the roughness and inhomogenieties of the solid surface [14]. In the absence and presence of the inhibiting molecules, the impedance spectra are characterized by two time constants; one at high frequency and the other at low frequency, both of which are generally attributed to the adsorption of intermediate species in case of the blank solution and inhibitor molecules with respect to the inhibiting solution onto the metal surface. Examination of the impedance plots clearly shows that the introduction of PPG into the corrodent affected the impedance responses of the system; notably an increase in the diameter of the semicircle (Fig. 2a), impedance modulus of the interface at the low frequency region (Fig. 2b).

![Figure 2: EIS plots for X60 steel in 15% HCl in the absence and presence of selected concentrations of PPG at PPG at 25 °C in (a) Nyquist and (b) Bode modulus formats](image)

EIS spectra for all tests were analyzed using the equivalent circuits shown in Fig. 3. In the equivalent circuit, CPE_{dl} element is considered as a model of double layer capacitance (R_{ct}) like water and other ion adsorbed on the surface of steel and CPE_{f} as a model of inhibitor film (R_{f}). Other parameters retain their usual meanings. In accordance with the equivalent circuit shown in Fig.3, the polarization resistance (R_{p}) is given as:

\[ R_p = R_{ct} + R_{f} \]  

(6)

where R_{ct} and R_{f} are charge transfer and inhibitor film resistances respectively.
The electrochemical impedance parameters viz. solution resistance ($R_s$), charge transfer resistance ($R_{ct}$), polarization resistance ($R_p$), double layer capacitance ($C_{dl}$), CPE exponents ($n$) obtained from the Nyquist plots and the calculated inhibition efficiency (IE%) are listed in Table 2. The inhibition efficiency and double layer capacitance were calculated using equations (7) and (8) respectively [15]:

$$IE(\%) = \left(1 - \frac{R_p^0}{R_p}\right) \times 100$$  \hspace{1cm} (5)

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_p}$$ \hspace{1cm} (6)

where $R_p^0$ and $R_p$ are the polarization resistance values in the absence and presence of the inhibitor respectively.

**Table 2**: Impedance parameters for X60 steel in 15% HCl without and with PPG at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>$R_s$ ($\Omega \text{ cm}^2$)</th>
<th>$Y_0$ (µΩs$^n$ cm$^{-2}$)</th>
<th>$n$</th>
<th>$R_f$ ($\Omega \text{ cm}^2$)</th>
<th>$Y_0$ (µΩs$^n$ cm$^{-2}$)</th>
<th>$n$</th>
<th>$R_{ct}$ ($\Omega \text{ cm}^2$)</th>
<th>$R_p$ ($\Omega \text{ cm}^2$)</th>
<th>$C_{dl}$ (µF cm$^{-2}$)</th>
<th>$\chi^2 \times 10^{-6}$</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.26</td>
<td>308.1</td>
<td>0.87</td>
<td>25.9</td>
<td>7071</td>
<td>0.59</td>
<td>11.8</td>
<td>37.7</td>
<td>169.7</td>
<td>58.1</td>
<td>–</td>
</tr>
<tr>
<td>50</td>
<td>2.09</td>
<td>44.4</td>
<td>0.89</td>
<td>21.4</td>
<td>528.8</td>
<td>0.54</td>
<td>168.7</td>
<td>190.1</td>
<td>67.5</td>
<td>84.4</td>
<td>80.2</td>
</tr>
<tr>
<td>100</td>
<td>1.14</td>
<td>39.3</td>
<td>0.89</td>
<td>25.4</td>
<td>551.7</td>
<td>0.56</td>
<td>189.9</td>
<td>215.3</td>
<td>93.1</td>
<td>83.4</td>
<td>82.5</td>
</tr>
<tr>
<td>200</td>
<td>1.52</td>
<td>35.1</td>
<td>0.89</td>
<td>24.5</td>
<td>312.5</td>
<td>0.59</td>
<td>272.8</td>
<td>297.8</td>
<td>67.3</td>
<td>81.4</td>
<td>87.4</td>
</tr>
<tr>
<td>500</td>
<td>1.16</td>
<td>31.8</td>
<td>0.89</td>
<td>32.1</td>
<td>479.3</td>
<td>0.49</td>
<td>345.7</td>
<td>377.8</td>
<td>66.7</td>
<td>25.9</td>
<td>90.0</td>
</tr>
<tr>
<td>1000</td>
<td>1.13</td>
<td>23.6</td>
<td>0.91</td>
<td>12.9</td>
<td>225.8</td>
<td>0.59</td>
<td>388.0</td>
<td>400.9</td>
<td>64.0</td>
<td>78.9</td>
<td>90.6</td>
</tr>
</tbody>
</table>

The results in Table 2 clearly show that in all cases, the $R_{ct}$ and $R_p$ increases with increase in concentration of PPG, corresponding to the increase in the diameter of the Nyquist semicircles. The values of inhibition efficiency (Table 2) are also observed to increase with increase in PPG concentration reaching the maximum value of 90.6% at
the optimum concentration of PPG (1000 ppm) studied. The result from this technique is in close agreement and follows the trend obtained from other electrochemical methods.

3.3 Weight loss measurements

Weight loss method was also employed to investigate the corrosion inhibition effect of PPG for X60 steel in 15% HCl solution. The result of the weight loss measurements at 25 °C after 24 h immersion time is presented in Table 3. It is evident from the table that the values of weight loss and corrosion rate decreased with increase in PPG concentration while the inhibition efficiency value increased. The decrease in both the weight loss and corrosion rate values is an indication that PPG inhibited the corrosion of X60 steel in the strong acid environment. The high degree of protection of X60 steel against corrosion by increasing the concentration of PPG is attributable to higher degree of surface coverage that resulted from enhanced PPG adsorption.

Table 3: Weight loss data for X60 steel in 15% HCl without and with different concentrations of PPG at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Weight loss ×10^{-2} (g)</th>
<th>Corrosion rate × 10^{-4} (g cm^{-2} h^{-1})</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>41.89</td>
<td>19.4</td>
<td>–</td>
</tr>
<tr>
<td>50</td>
<td>8.91</td>
<td>4.13</td>
<td>78.8</td>
</tr>
<tr>
<td>100</td>
<td>6.70</td>
<td>3.10</td>
<td>84.0</td>
</tr>
<tr>
<td>200</td>
<td>6.24</td>
<td>2.89</td>
<td>85.1</td>
</tr>
<tr>
<td>500</td>
<td>5.89</td>
<td>2.73</td>
<td>85.9</td>
</tr>
<tr>
<td>1000</td>
<td>4.99</td>
<td>2.31</td>
<td>88.1</td>
</tr>
</tbody>
</table>

3.4 Effect of immersion time on inhibition by PPG

The impedance response for X60 steel in 15% HCl in the absence and presence of 1000 ppm PPG at different immersion times at 25 °C is shown in Fig. 4 in (a) Nyquist and (b) Bode modulus representations. Some important electrochemical impedance parameters derived from the Nyquist diagrams are listed in Table 4. Inspection of Fig. 4 clearly shows that increase in immersion time did not change the mechanism of the corrosion process in the presence of PPG as the shape of the Nyquist plots in its presence and absence remains unchanged. The Nyquist plots are characterized by two time constants hence the equivalent circuit shown in Fig. 3 was also used to fit the Nyquist plot to obtain impedance data of interest. The diameter of the semicircles in the Nyquist and the magnitude of the Bode modulus in the low frequency region are observed to decrease with increase in immersion time. It is evident from the data in Table 4 that $R_{ct}$ and $R_p$ values of the steel in 15% HCl containing 1000 ppm PPG decreased with prolonged immersion time up to 96 h, however, the charge transfer and polarization resistances under these conditions are still large enough as compared with the blank solution. Also the IE (%) is observed to diminish linearly with immersion time.
The decrease in IE with increase immersion time for corrosion inhibitors in acid media has been reported by some researchers [16]. Decreased IE with prolonged immersion time is often attributed to either non-uniformity and instability of the adsorptive film or the desorption of the adsorbed inhibitor from the metal’s surface. It is worthy to mention that PPG is an effective corrosion inhibitor for X60 steel in 15% HCl solution as it can provide protection (IE = 70%) to the steel substrate after 96 h exposure to this highly aggressive corrosion environment.

Figure 4: EIS plots for X60 steel in 15% HCl in the absence and presence of 1000 ppm PPG at different immersion times at 25 °C in (a) Nyquist and (b) Bode modulus formats

Table 4: Important impedance parameters for X60 steel in 15% HCl without and with 1000 ppm PPG at different immersion times at 25 °C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$f_{\text{max}}$ (Hz)</th>
<th>$R_{\text{ct}}$ (Ω cm$^2$)</th>
<th>$R_{\text{l}}$ (Ω cm$^2$)</th>
<th>$R_{\text{p}}$ (Ω cm$^2$)</th>
<th>$C_{\text{dl}}$ (µF cm$^{-2}$)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>24.93</td>
<td>11.8</td>
<td>25.9</td>
<td>37.7</td>
<td>169.7</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>6.20</td>
<td>388.0</td>
<td>12.9</td>
<td>400.9</td>
<td>64.0</td>
<td>90.6</td>
</tr>
<tr>
<td>4</td>
<td>6.31</td>
<td>223.0</td>
<td>21.9</td>
<td>244.9</td>
<td>112.4</td>
<td>84.7</td>
</tr>
<tr>
<td>8</td>
<td>5.00</td>
<td>202.5</td>
<td>21.9</td>
<td>224.4</td>
<td>141.8</td>
<td>83.2</td>
</tr>
<tr>
<td>24</td>
<td>2.50</td>
<td>179.8</td>
<td>19.8</td>
<td>199.6</td>
<td>318.9</td>
<td>81.2</td>
</tr>
<tr>
<td>72</td>
<td>0.79</td>
<td>152.4</td>
<td>3.5</td>
<td>155.9</td>
<td>1291.2</td>
<td>75.9</td>
</tr>
<tr>
<td>96</td>
<td>0.79</td>
<td>123.9</td>
<td>2.6</td>
<td>126.5</td>
<td>1592.2</td>
<td>70.3</td>
</tr>
</tbody>
</table>

3.5 Adsorption consideration

The degree of surface coverage ($\theta$) values obtained from different techniques were theoretically fitted to different adsorption isotherm models in order to determine more accurately which isotherm best described the adsorption of PPG onto X60 steel surface in the strong acid medium. The degree of surface coverage was obtained as follows: $\theta = \text{IE}/100$ (assuming a direct relationship between surface coverage ($\theta$) and
inhibition efficiency (IE (%)). The plot of C/θ vs C is shown in Fig. 5 to be linear with very good correlation coefficient \( R^2 \) (close to unity). This indicates that Langmuir adsorption isotherm is obeyed and that the adsorption of PPG on X60 steel surface can be approximated by Langmuir adsorption isotherm model.

![Graph showing Langmuir adsorption isotherm](image)

**Figure 5**: Langmuir adsorption isotherm for X60 steel in 15% HCl containing PPG from the different experimental techniques

Langmuir isotherm is characterized by:

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{7}
\]

where C is the concentration, θ is the degree of surface coverage and \( K_{ads} \) is the equilibrium constant of the adsorption-desorption process. The adsorption parameters derived from the Langmuir plots are listed in Table 5.

**Table 5**: Langmuir adsorption parameters for X60 steel in 15% HCl containing PPG from different experimental techniques at 25 °C.

<table>
<thead>
<tr>
<th>Methods</th>
<th>( \Delta G_{ads}^0 ) (kJ mol(^{-1}))</th>
<th>( K_{ads} ) (L mg(^{-1}))</th>
<th>slope</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>WL</td>
<td>28.92</td>
<td>0.1175</td>
<td>1.13</td>
<td>0.999</td>
</tr>
<tr>
<td>EIS</td>
<td>27.01</td>
<td>0.0543</td>
<td>1.09</td>
<td>0.999</td>
</tr>
<tr>
<td>LPR</td>
<td>28.56</td>
<td>0.1061</td>
<td>1.08</td>
<td>0.999</td>
</tr>
<tr>
<td>PDP</td>
<td>29.18</td>
<td>0.1301</td>
<td>1.05</td>
<td>0.999</td>
</tr>
</tbody>
</table>

The slopes from all the experimental techniques are unity meaning that PPG interacts significantly with the metallic surface to form a monolayer film over the metal surface. From the value of adsorption-desorption constant, \( K_{ads} \), the standard free energy of adsorption was obtained as follows [17]:

\[
\Delta G_{ads}^0 = -RT \ln \left( 1 \times 10^6 K_{ads} \right) \tag{8}
\]
where \( R \) is the universal constant, \( T \) is the absolute temperature and \( 1 \times 10^6 \) is the concentration of water molecules expressed in mg L\(^{-1}\). The values of \( \Delta G^\circ_{\text{ads}} \) obtained from the different methods are listed in Table 5 is found to lie between \(-27.01\) and \(-29.18\) kJ.mol. These values are more negative than \(-20\) kJ mol (threshold value for physisorption) less negative than \(-40\) kJ/mol (threshold value for chemisorption), hence adsorption of PPG on the metal surface could be ascribed to comprehensive adsorption.

### 3.6 Effect of Temperature

Effect of temperature on the corrosion and corrosion inhibition of X60 steel without and with PPG was assessed using weight loss measurements at the temperature range of 25 – 60 °C using selected concentration (50, 200 and 1000 ppm) of PPG. The result obtained for 24 h immersion period is presented in Table 6. It is clear from the table that corrosion rates of X60 steel in 15 % HCl in the absence and presence PPG increased with increase in temperature. Further inspection of the table reveals that inhibition efficiency increased with increase in temperature up to 55 °C and thereafter the inhibition efficiency decreased as temperature was raised to 60 °C.

**Table 6**: Weight loss data for X60 steel in 15% HCl without and with selected concentration of PPG at different temperatures

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Corrosion rate ( \times 10^{-4} ) (g cm(^{-2}) h(^{-1}))</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>40 °C</td>
</tr>
<tr>
<td>Blank</td>
<td>19.4</td>
<td>67.57</td>
</tr>
<tr>
<td>50</td>
<td>4.13</td>
<td>9.49</td>
</tr>
<tr>
<td>200</td>
<td>2.89</td>
<td>8.46</td>
</tr>
<tr>
<td>1000</td>
<td>2.31</td>
<td>7.25</td>
</tr>
</tbody>
</table>

The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation:

\[
\log C_R = \log A - \frac{E_a}{2.303RT}
\]

(9)

where \( C_R \) is the corrosion rate, \( E_a \) is the apparent activation energy, \( R \) is the molar gas constant, \( T \) is the absolute temperature, and \( A \) is the frequency factor. The plot of \( \log C_R \) against \( 1/T \) (Fig.6a) is shown to be linear indicating that Arrhenius equation is obeyed. The apparent activation energy (\( E_a \)) values derived from the slope of the Arrhenius plots are displayed in Table 7. It is seen from the table that \( E_a \) in the presence of PPG is less than that in the blank solution. This is usually the case when the inhibition efficiency is found to increase with increase in temperature (as in the present
study) and some authors largely attributed it to specific interactions between the inhibitor and the metal surface [18].

The activation enthalpy and entropy of corrosion for the X60 steel – HCl system without and with PPG were obtained from the equation of the Transition State Theory given by:

$$
\log \left( \frac{C_R}{T} \right) = \left[ \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S^*}{2.303R} \right) \right] - \frac{\Delta H^*}{2.303RT}
$$

where \( h (6.626176 \times 10^{-34} \text{Js}) \) is the Planck’s constant, \( N (6.02252 \times 10^{23} \text{mol}^{-1}) \) is the Avogadro’s number, \( R \) and \( T \) retain the earlier meanings. Figure 6b presents the Transition State plots as \( \log (C_R/T) \) against \( 1/T \) for X60 steel corrosion in 15% HCl solution without and with PPG. Straight line graphs were obtained with slope of \( -\Delta H^*/2.303R \) and intercept of \( \log (R/Nh) + (\Delta S^*/2.303R) \) from which the values of \( \Delta H^* \) and \( \Delta S^* \), respectively, were calculated and listed in Table 7.

**Table 7**: Activation parameters from transition state plot for X60 steel in 15% HCl in the absence and presence of selected concentrations of PPG.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>( \Delta H^* ) (kJ mol(^{-1}))</th>
<th>( -\Delta S^* ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>61.55</td>
<td>59.67</td>
<td>96.45</td>
</tr>
<tr>
<td>50</td>
<td>54.01</td>
<td>51.32</td>
<td>137.50</td>
</tr>
<tr>
<td>200</td>
<td>59.42</td>
<td>56.66</td>
<td>122.79</td>
</tr>
<tr>
<td>1000</td>
<td>60.84</td>
<td>57.71</td>
<td>120.96</td>
</tr>
</tbody>
</table>

From the table, it is seen that the values \( \Delta H^* \) are close to that of \( E_a \) as expected from the concept of transition state theory and follow the same pattern of variation with concentration of PPG. It could also be seen from the table that \( \Delta S^* \) values are large.
and negative indicating that the activated complex in the rate determining step represents an association rather than dissociation.

### 3.7 Surface analysis

Fig. 7(a)–(c) depicts the morphologies of X60 abraded and samples after immersion for 24 h in 15% HCl solution without and with 1000 ppm of PPG. It is clearly observed that the surface of X60 in the blank (Fig. 7(b)) is seriously damaged as compared to the pre-immersion sample (Fig. 7(a)). In the presence of the PPG, the extent of damage of the steel surface is significantly reduced (Fig. 7(c)). This demonstrates that the PPG has formed a protective film on the X60 steel surface and as a result reduced the extent of corrosion.

Fig. 8 shows the water contact angles images for X60 steel (a) in the polished state (b) exposed to 15% HCl and (c) exposed to 15% HCl containing 1000 ppm PPG after 24 h. The water contact angle for the uncorroded X60 steel was 89.86° (Fig.8a). It is clear from the figure that exposure to 15% HCl solution causes the contact angle to decrease to 24.15°, i.e. the surface show an increased affinity for water compared to the unexposed X60 steel sample. This could be attributed to the roughness of the surface due excessive acid attack as well as formation of polar inorganic corrosion products on the steel surface, thus increasing its wettability.

![Figure 7](image1.png)

**Figure 7:** SEM micrographs for X60 steel (a) in the polished state (b) exposed to 15% HCl and (c) exposed to 15% HCl containing 1000 ppm PPG after 24 h.

![Figure 8](image2.png)

**Figure 8:** Water contact images for X60 steel (a) in the polished state (b) exposed to 15% HCl and (c) exposed to 15% HCl containing 1000 ppm PPG after 24 h.
4. Conclusions

The following conclusions could be drawn from the work based on experimental findings:

1. Polypropylene glycol (PPG) is found to inhibit the corrosion of X60 pipeline steel in 15% HCl solution. The inhibition effect is concentration dependent.
2. Inhibition efficiency increased with increase in concentration of PPG and temperature up to 55 °C but decreased with increase in immersion time and temperature up to 60 °C.
3. Corrosion inhibition is afforded by virtue of adsorption of PPG molecules onto X60 steel surface which can be approximated by Langmuir adsorption isotherm model.
4. The results of potential dynamic polarization measurements indicate that PPG behaved as a mixed inhibitor affecting both cathodic hydrogen evolution and anodic X60 steel dissolution reactions.
5. The phenomenon of comprehensive adsorption (both physisorption and chemisorption) is proposed from the trend of inhibition efficiency with temperature and the values of kinetic/thermodynamic parameters obtained from the experimental data.
6. SEM surface analysis and water contact angles measurements results are in good agreement and points clearly to the fact that PPG functions as inhibitor by virtue of adsorption onto the metal surface.

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References


