Research Article

Study of Temperature Effect on the Corrosion Inhibition of C38 Carbon Steel Using Amino-tris(Methyleneophosphonic) Acid in Hydrochloric Acid Solution

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Tafel polarization method was used to assess the corrosion inhibitive and adsorption behaviours of amino-tris(methyleneophosphonic) acid (ATMP) for C38 carbon steel in 1 M HCl solution in the temperature range from 30 to 60°C. It was shown that the corrosion inhibition efficiency was found to increase with increase in ATMP concentration but decreased with temperature, which is suggestive of physical adsorption mechanism. The adsorption of the ATMP onto the C38 steel surface was found to follow Langmuir adsorption isotherm model. The corrosion inhibition mechanism was further corroborated by the values of kinetic and thermodynamic parameters obtained from the experimental data.

1. Introduction

Corrosion inhibition of steel in acid solutions by different types of inhibitors has been extensively studied. The use of environmentally acceptable inhibitors is favoured. Phosphonates are known to be environmentally friendly corrosion inhibitors, which form adsorbed layers on oxide- or hydroxide-covered metal surfaces [1–4]. Many works can be found in the literature about the interactions between phosphonates and iron or steels. In particular, Ochoa and al. [2, 4] studied the interaction between phosphonocarboxylic acid salts (monophosphonates) and carbon steel. Their environmental impact at usual concentrations for corrosion inhibition is negligible [5, 6]. Moreover, in contrast to inorganic phosphorous compounds, they do not cause eutrophication. Their high stability to hydrolysis and resistance to degradation is also beneficial. It was found that few inhibitors with acid-metal systems have specific reactions that are still effective at high temperatures as (or more) they are at low temperatures [7, 8]. A large number of investigations have studied the temperature effects on acidic corrosion and corrosion inhibition of iron and steel in HCl and H2SO4 solutions [9–17].

In previous work [1], the improving of the corrosion resistance of C38 carbon steel in 1 M HCl solution using ATMP has been investigated at 30°C by means of gravimetric and electrochemical (ac impedance and Tafel polarisation) methods. We have found that this compound is efficient inhibitor in 1 M HCl and the corrosion inhibition is mainly controlled by a physisorption process. The antibacterial activity investigations have been shown that the ATMP has an antibacterial effect against both Gram-positive and Gram-negative bacteria [1]. A great limitation of the inhibitor application is the fall down of their efficiencies at high temperatures. The effect of temperature on the inhibited acid-metal reaction is highly complex because many charges...
occur on the metal surface such as rapid etching and desorption of the inhibitor, and the inhibitor itself, in some cases, may undergo decomposition and/or rearrangement [18]. However, it provides the ability of calculating many thermodynamic functions for the inhibition and/or the adsorption processes which contribute in determining the type of adsorption of the studied inhibitor. The aim of this work is then to study the effect of temperature on C38 carbon steel corrosion process in 1 M HCl both in the absence and in the presence of amino-tris(methyleneephosphonic) acid-(ATMP) using Tafel polarisation method. The thermodynamic parameters for both activation and adsorption processes were calculated and discussed.

2. Experimental Details

The material used in this study is a C38 carbon steel with a chemical composition (in wt.%) of 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% Cu, and the remainder iron (Fe). The C38 carbon samples were pretreated prior to the experiments by grinding with emery paper SiC (120, 600, and 1200), rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water, and then dried at room temperature before use. The tested compound, namely amino-tris(methyleneephosphonic) acid (ATMP), obtained from Sigma-Aldrich (50 wt.% in H2O), was tested without further purification. The molecular structure of the ATMP is shown in Figure 1. The acid solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water.

Polarisation curves were conducted using an electrochemical measurement system Tacussel-Radiometer model PGZ 301 potentiostat controlled by a PC and supported by Voltamaster 4.0 software. Electrochemical measurements were carried out in a conventional three-electrode cylindrical Pyrex glass cell. The temperature is thermostatically controlled. The working electrode (WE) in the form of disc cut from steel has a geometric area of 1 cm2 and is embedded in polytetrafluoroethylene (PTFE). A saturated calomel electrode (SCE) and a platinum electrode were used, as reference and auxiliary electrodes, respectively. A fine Luggin capillary was placed close to the working electrode to mini-mize IR drop. All test solutions were deaerated in the cell by using pure nitrogen for 10 min prior to the experiment. During each experiment, the test solution was mixed with a magnetic stirrer, and the gas bubbling was maintained. The mild steel electrode was maintained at corrosion potential for 30 min and thereafter prepolared at −800 mV SCE for 10 min. The potentiodynamic current potential curves were obtained by changing the electrode potential automatically from −800 to −200 mV SCE with a scan rate of 0.5 mV s−1.

3. Results and Discussion

3.1. Corrosion Kinetic Study. In order to gain more information about the type of adsorption and the effectiveness of the ATMP inhibitor at higher temperature, polarisation experiment was conducted in the range of 30–60°C without and with selected concentrations of the inhibitor. Representative Tafel polarisation curves for C38 steel electrode in 1 M HCl without and with 0.1 M of ATMP at different temperatures are shown in Figure 2. Similar polarisation curves were obtained in the case of the other concentrations of ATMP (not given). The analysis of these figures reveals that raising the temperature increases both anodic and cathodic current densities, and consequently the corrosion rate of C38 steel increases.

Electrochemical kinetic parameters (corrosion potential (Ecorr), corrosion current density (Icorr), and cathodic Tafel slope (b)), determined from these experiments by extrapolation method [19–23], are reported in Table 1. The Icorr was determined by Tafel extrapolation of only the cathodic polarization curve alone, which usually produces a longer and better defined Tafel region [24]. The inhibition efficiencies, E(%), are calculated from Icorr values as described elsewhere [18]. The surface coverage θ was calculated from the following equation [25]:

\[ \theta = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}} - I_{\text{sat}}} \] (1)

where Icorr, Icorr(inh), and Isat are the corrosion current density values in the absence, the presence of ATMP, and in an entirely covered surface, respectively. (Isat = Icorr for the most elevated concentration of inhibitor). As Isat ≪ Icorr, thus

\[ \theta = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \] (2)

Analyse of the results in Table 1 indicates that in the presence of ATMP molecules, the Icorr of C38 steel decreases at any given temperature as inhibitor concentration increases compared to the uninhibited solution, due to the increase of the surface coverage degree. In contrast, at constant ATMP concentration, the Icorr increases as temperature rises, but this increase is more pronounced for the blank solution. Hence we can note that the E(%) depends on the temperature and decreases with the rise of temperature from 30 to

![Figure 1: Molecular structure of the amino-tris(methyleneephosphonic) acid (ATMP).](image-url)
60°C. This can be explained by the decrease of the strength of the adsorption process at elevated temperature and would suggest a physical adsorption mode.

The activation parameters for the corrosion reaction can be regarded as an Arrhenius-type process, according to the following equation:

\[ I_{\text{corr}} = A \exp \left( -\frac{E_a}{RT} \right) , \]

where \( E_a \) is the apparent activation corrosion energy, \( R \) is the universal gas constant, and \( A \) is the Arrhenius preexponential factor. The apparent activation energies \( (E_a) \) in the absence and in the presence of various concentrations of ATMP are calculated by linear regression between \( \ln \left( I_{\text{corr}} \right) \) and \( 1/T \) (Figure 3), and the results are given in Table 2. All the linear regression coefficients are close to 1, indicating that the steel corrosion in hydrochloric acid can be elucidated using the kinetic model. As observed from Table 2, the \( E_a \) increased with increasing concentration of ATMP, but all values of \( E_a \) in the range of the studied concentration were higher than that of the uninhibited solution. The increase in \( E_a \) in the presence of ATMP may be interpreted as physical adsorption. Indeed, a higher energy barrier for the corrosion process in the inhibited solution is associated with physical adsorption or weak chemical bonding between the inhibitor species and the steel surface [14, 26]. Sauer and Brand. explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the carbon steel surface with the increase in temperature. A corresponding increase in the corrosion rate occurs because of the greater area of metal that is consequently exposed to the acid environment [27].

The enthalpy of activation \( (\Delta H_a) \) and the entropy of activation \( (\Delta S_a) \) for the intermediate complex in the transition state for the corrosion of C38 steel in 1 M HCl in the absence and in the presence of different concentrations of ATMP were obtained by applying the alternative formulation of Arrhenius equation [28]:

\[ I_{\text{corr}} = \frac{RT}{Nh} \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( -\frac{\Delta H_a}{RT} \right) , \]

where \( h \) is the Plank’s constant and \( N \) is the Avogadro’s number. Figure 4 shows a plot of \( \ln(I_{\text{corr}}/T) \) versus \( 1/T \). A straight line is obtained with a slope of \( (-\Delta H_a/R) \) and an intercept of \( (\ln R/\Delta S_a/R) \) from which the values of \( \Delta H_a \) and \( \Delta S_a \) were calculated (Table 2). The positive values of \( \Delta H_a \) in the absence and the presence of ATMP reflect the endothermic nature of the C38 steel dissolution process. One can also notice that \( E_a \) and \( \Delta H_a \) values vary in the same way.

### Table 1: Electrochemical parameters and the corresponding inhibition efficiencies at various temperatures studied of C38 steel in 1 M HCl containing different concentrations of ATMP.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conc. (M)</th>
<th>( E_{\text{corr}} ) versus SCE mV</th>
<th>( I_{\text{corr}} ) (μA cm(^{-2}))</th>
<th>( b_c ) (mV dec(^{-1}))</th>
<th>( E ) (%)</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1 M HCl</td>
<td>-482</td>
<td>569.8</td>
<td>188</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>5 × 10^{-5}</td>
<td>-482</td>
<td>477.8</td>
<td>186</td>
<td>16.1</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>5 × 10^{-3}</td>
<td>-473</td>
<td>175.4</td>
<td>146</td>
<td>69.2</td>
<td>0.69</td>
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<tr>
<td></td>
<td>5 × 10^{-2}</td>
<td>-471</td>
<td>109.3</td>
<td>128</td>
<td>80.8</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>1 × 10^{-1}</td>
<td>-464</td>
<td>76.7</td>
<td>122</td>
<td>86.5</td>
<td>0.87</td>
</tr>
<tr>
<td>40</td>
<td>1 M HCl</td>
<td>-464</td>
<td>800.7</td>
<td>190</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>5 × 10^{-5}</td>
<td>-470</td>
<td>700.3</td>
<td>189</td>
<td>12.5</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>5 × 10^{-3}</td>
<td>-452</td>
<td>478.7</td>
<td>154</td>
<td>40.2</td>
<td>0.40</td>
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<tr>
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<td>5 × 10^{-2}</td>
<td>-471</td>
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<td>132</td>
<td>61.5</td>
<td>0.61</td>
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<tr>
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<td>-462</td>
<td>235.3</td>
<td>129</td>
<td>70.6</td>
<td>0.71</td>
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<tr>
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<td>1 M HCl</td>
<td>-461</td>
<td>999.1</td>
<td>191</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>5 × 10^{-5}</td>
<td>-455</td>
<td>875.9</td>
<td>188</td>
<td>12.3</td>
<td>0.12</td>
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<tr>
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<td>5 × 10^{-3}</td>
<td>-463</td>
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<td>166</td>
<td>26.2</td>
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<td>134</td>
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<td>0.59</td>
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<tr>
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<td>1 M HCl</td>
<td>-465</td>
<td>1314.7</td>
<td>194</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
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<td>5 × 10^{-5}</td>
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<td>9.0</td>
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<td>20.4</td>
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<td>40.1</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>1 × 10^{-1}</td>
<td>-445</td>
<td>651.1</td>
<td>152</td>
<td>50.5</td>
<td>0.50</td>
</tr>
</tbody>
</table>

### Table 2: Corrosion kinetic parameters for C38 steel in 1 M HCl in absence and presence of different concentrations of ATMP.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>( \Delta H_a ) (kJ mol(^{-1}))</th>
<th>( \Delta S_a ) (J mol(^{-1}) K(^{-1}))</th>
<th>( E_a - \Delta H_a ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>22.92</td>
<td>20.28</td>
<td>-125.22</td>
<td>2.64</td>
</tr>
<tr>
<td>5 × 10^{-5}</td>
<td>24.98</td>
<td>22.34</td>
<td>-119.84</td>
<td>2.64</td>
</tr>
<tr>
<td>5 × 10^{-3}</td>
<td>48.90</td>
<td>46.26</td>
<td>-48.05</td>
<td>2.64</td>
</tr>
<tr>
<td>5 × 10^{-2}</td>
<td>55.25</td>
<td>52.62</td>
<td>-31.04</td>
<td>2.63</td>
</tr>
<tr>
<td>1 × 10^{-1}</td>
<td>58.75</td>
<td>56.11</td>
<td>-22.43</td>
<td>2.64</td>
</tr>
</tbody>
</table>
The well-known thermodynamic adsorption parameters are the free energy of adsorption \((\Delta G_{ads})\), the standard enthalpy of adsorption \((\Delta H_{ads})\), and the entropy of adsorption \((\Delta S_{ads})\). These quantities can be calculated depending on the estimated values of \(K_{ads}\) from adsorption isotherms, at different temperatures. The constant of adsorption, \(K_{ads}\), is related to the standard free energy of adsorption, \(\Delta G_{ads}^0\), with the following equation \([34]\):

\[
K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right),
\]

where \(\Delta G_{ads}^0\) and the water molecules on the metallic surface \(H_2O(ads)\),

\[
\text{Org}_{(sol)} + n \text{H}_2\text{O}_{(ads)} \rightleftharpoons \text{Org}_{(ads)} + n \text{H}_2\text{O}_{(sol)},
\]

and the water molecules on the metallic surface \(H_2O(ads)\),

\[
\text{Org}_{(sol)} + n \text{H}_2\text{O}_{(ads)} \rightleftharpoons \text{Org}_{(ads)} + n \text{H}_2\text{O}_{(sol)},
\]

and the water molecules on the metallic surface \(H_2O(ads)\),

\[
\text{Org}_{(sol)} + n \text{H}_2\text{O}_{(ads)} \rightleftharpoons \text{Org}_{(ads)} + n \text{H}_2\text{O}_{(sol)},
\]

and the water molecules on the metallic surface \(H_2O(ads)\),

\[
\text{Org}_{(sol)} + n \text{H}_2\text{O}_{(ads)} \rightleftharpoons \text{Org}_{(ads)} + n \text{H}_2\text{O}_{(sol)},
\]

and the water molecules on the metallic surface \(H_2O(ads)\),

\[
\text{Org}_{(sol)} + n \text{H}_2\text{O}_{(ads)} \rightleftharpoons \text{Org}_{(ads)} + n \text{H}_2\text{O}_{(sol)},
\]

and the water molecules on the metallic surface \(H_2O(ads)\),

\[
\text{Org}_{(sol)} + n \text{H}_2\text{O}_{(ads)} \rightleftharpoons \text{Org}_{(ads)} + n \text{H}_2\text{O}_{(sol)},
\]
The obtained values of $\Delta G_{ads}^o$ show a regular dependence on temperature, indicating a good correlation among thermodynamic parameters. However, a limited decrease in the absolute value of $\Delta G_{ads}^o$ with the increase in temperature values is observed. This behaviour is explained by the fact that the adsorption is somewhat unfavourable with increasing experimental temperature, indicating that the physisorption has the major contribution while the chemisorption has a minor contribution in the corrosion inhibition mechanism [37]. The other thermodynamic functions ($\Delta H_{ads}^o$ and $\Delta S_{ads}^o$) can be calculated from the following equation:

$$\Delta G_{ads}^o = \Delta H_{ads}^o - T\Delta S_{ads}^o.$$  

Figure 6 shows the plot of $\Delta G_{ads}^o$ versus $T$ which gives straight lines with slopes of $-\Delta S_{ads}^o$ and intercepts of $\Delta H_{ads}^o$. The obtained values of $\Delta H_{ads}^o$ and $\Delta S_{ads}^o$ are given in Table 3. The obtained value of $\Delta H_{ads}^o$ is negative, reflecting the exothermic nature of the adsorption process on C38 steel surface. The value of $\Delta H_{ads}^o$ can also provide valuable information about the type of inhibitor adsorption. While an endothermic adsorption process ($\Delta H_{ads}^o > 0$) is attributed unequivocally to chemisorption [38], an exothermic adsorption process ($\Delta H_{ads}^o < 0$) may involve either physisorption or chemisorption or a mixture of both the processes. In an exothermic process, chemisorption is distinguished from physisorption by considering the absolute value of $\Delta H_{ads}^o$. For the chemisorption process, $\Delta H_{ads}^o$ approaches 100 kJ mol$^{-1}$, while for the physisorption process, it is less than 40 kJ mol$^{-1}$ [37]. In the case of ATMP, the calculated value of $\Delta H_{ads}^o (-56.56$ kJ mol$^{-1}$) is larger than the common physical adsorption enthalpy, but smaller than the common-chemical adsorption enthalpy, confirming that the adsorption mechanism of ATMP on carbon steel surface probably involves two types of interactions, predominant physisorption (ionic), and weak chemisorption (molecular). The value of $\Delta S_{ads}^o$ is negative (Table 3), meaning that the inhibitor

where $R$ is the universal gas constant, $T$ is the thermodynamic temperature, and the value of 55.5 is the concentration of water in the solution in mol/L. The calculated $\Delta G_{ads}^o$ values, at all studied temperatures, are given in Table 3. The negative values of $\Delta G_{ads}^o$ indicate the spontaneity of the adsorption process and the stability of the adsorbed layer on the 38C steel surface [16]. Generally, the adsorption type is regarded as physisorption if the absolute value of $\Delta G_{ads}^o$ is in the range of 20 kJ mol$^{-1}$ or lower. The inhibition behaviour is attributed to the electrostatic interaction between the organic molecules and steel surface. When the absolute value of $\Delta G_{ads}^o$ is in the order of 40 kJ mol$^{-1}$ or higher, the adsorption could be seen as chemisorption. In this process, the covalent bond is formed by the charge sharing or transferring from the inhibitor molecules to the metal surface [35, 36]. The obtained $\Delta G_{ads}^o$ values in the studied temperature domain are in the range of $-23.5$ to $-26.5$ kJ mol$^{-1}$, indicating, therefore, that the adsorption mechanism of the ATMP onto C38 steel in 1 M HCl solution is mainly due to physisorption (Table 3). This behaviour is in good agreement with that obtained at 30°C using ac impedance technique [1]. On the other hand, the obtained values of $\Delta G_{ads}^o$ show a regular dependence on temperature, indicating a good correlation among thermodynamic parameters. However, a limited decrease in the absolute value of $\Delta G_{ads}^o$ with the increase in temperature values is observed. This behaviour is explained by the fact that the adsorption is somewhat unfavourable with increasing experimental temperature, indicating that the physisorption has the major contribution while the chemisorption has a minor contribution in the corrosion inhibition mechanism [37]. The other thermodynamic functions ($\Delta H_{ads}^o$ and $\Delta S_{ads}^o$) can be calculated from the following equation:

$$\Delta G_{ads}^o = \Delta H_{ads}^o - T\Delta S_{ads}^o.$$  

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molecules move freely in the bulk solution (are chaotic) before adsorption, while as adsorption progresses, the inhibitor molecules adsorbed onto the mild steel surface become more orderly, resulting in a decrease in entropy [39].

\[
\Delta H_{\text{ads}}^o \text{ and } \Delta S_{\text{ads}}^o \text{ can be also deduced from the integrated version of the Van't Hoff equation expressed by [40]}
\]

\[
\ln K_{\text{ads}} = -\frac{\Delta H_{\text{ads}}^o}{RT} + \text{constant.} \tag{11}
\]

Figure 7 shows the plot of \( \ln K_{\text{ads}} \) versus \( 1/T \) which gives straight lines with slopes of \( (-\Delta H_{\text{ads}}^o/R) \) and intercepts of \( (\Delta S_{\text{ads}}^o/R + \ln 1/55.5) \). The calculated \( \Delta H_{\text{ads}}^o \) using the Van’t Hoff equation is \(-55.55 \text{ kJ mol}^{-1}\) for ATMP, confirming the physisorption process and the exothermic behaviour of the adsorption of the ATMP molecule on the steel surface. Values of \( \Delta H_{\text{ads}}^o \) obtained by both methods are in good agreement. Moreover, the deduced \( \Delta S_{\text{ads}}^o \) value of \(-97.16 \text{ J mol}^{-1}\text{K}^{-1} \) for ATMP is very close to that obtained in Table 3.

4. Conclusion
We studied the inhibitor action of ATMP on corrosion of C38 steel in 1 M HCl depending on effect of temperature. We obtained the following conclusion.

(1) Based on the Tafel polarization results, the \( E \% \) of ATMP is found to decrease with increasing temperature, and its addition to 1 M HCl leads to an increase of apparent activation energy \( (E_a) \) of the corrosion process.

(2) The corrosion process is inhibited by the adsorption of ATMP on C38 steel surface. This adsorption fits a Langmuir isotherm model. Thermodynamic adsorption parameters show that ATMP is adsorbed on steel surface by an exothermic and spontaneous process.

(3) The calculated values of \( \Delta G_{\text{ads}} \) and \( \Delta H_{\text{ads}}^o \) corroborate that the adsorption mechanism of ATMP on steel surface in 1 M HCl solution is mainly due to physisorption.

(4) At temperatures higher than 30°C, this inhibitor is not efficient to control the corrosion of steel in 1 M HCl at the concentration range studied.

### Table 3: Thermodynamic parameters for the adsorption of ATMP on the C38 steel in 1 M HCl at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( R^2 )</th>
<th>( K_{\text{ads}} ) (M(^{-1}))</th>
<th>( \Delta G_{\text{ads}}^o ) (kJ mol(^{-1}))</th>
<th>( \Delta H_{\text{ads}}^o ) (kJ mol(^{-1}))</th>
<th>( \Delta S_{\text{ads}}^o ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.99</td>
<td>666.7</td>
<td>-26.50</td>
<td>-54.87</td>
<td>-95.00</td>
</tr>
<tr>
<td>40</td>
<td>0.99</td>
<td>222.2</td>
<td>-24.52</td>
<td>-54.87</td>
<td>-95.00</td>
</tr>
<tr>
<td>50</td>
<td>0.99</td>
<td>138.9</td>
<td>-24.04</td>
<td>-54.87</td>
<td>-95.00</td>
</tr>
<tr>
<td>60</td>
<td>0.98</td>
<td>86.9</td>
<td>-23.49</td>
<td>-54.87</td>
<td>-95.00</td>
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References


