Evaluation of Chitosan and Carboxymethyl Cellulose (CMC) as Ecofriendly Corrosion Inhibitors for X60 Pipeline Steel in CO$_2$ Saturated 3.5% NaCl Solution

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Summary

One of the cost-effective methods for controlling carbon steel corrosion in the oil and gas production is the use of chemical corrosion inhibition. However, there is an increasing need in the industry to limit the use of chemicals, mainly due to more severe environmental impact, and current research are focused on search for greener alternatives. In this study, the performance of two green inhibitors; chitosan and carboxymethyl cellulose (CMC), on a typical X60 pipeline steel in CO$_2$ saturated 3.5% NaCl solution were investigated in both static and dynamic conditions using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) techniques. Also, metal surface characterization was performed using scanning electron microscope (SEM). The results indicate that there is a remarkable difference in inhibition efficiency of each inhibitor on the low carbon X60 steel. Inhibition efficiency increased with the increase of Chitosan and CMC concentrations. Immersion time was found to have a profound effect on the corrosion inhibition performance of each inhibitor. Even though the inhibition efficiency decreased with the increase in temperature, still both Chitosan and CMC act as good corrosion inhibitors for X60 steel. The rotating cylinder electrode (RCE) was used to study the rate of corrosion under high velocity (high shear, turbulent) flow conditions and the results revealed that the inhibition efficiency of Chitosan decreased in the dynamic condition while the same increased for CMC. Potentiodynamic polarization results (not included in this report for lack of space), reveal a mixed-type inhibition for both systems of inhibitors. The adsorption of each inhibitor on the steel surface obeys Langmuir’s isotherm.

**Keywords:** Green Inhibitors, Chitosan, Carboxymethyl Cellulose, Sweet Corrosion, Low Carbon X60 Steel, Rotating Cylinder Electrode.

Introduction

Carbon steels are widely used in the oil and gas industry for different purposes and they are hugely susceptible corrosion in the service environment to which they are deployed thereby limiting their end-use. The most frequent aggressive environments found in the petroleum industry are those of fluids with high concentrations of chlorides containing carbon dioxide (CO$_2$) [1]. CO$_2$ corrosion involves the interaction of the gas with steel and
water, and one of the cost-effective methods for controlling this corrosion type is by the use of chemical corrosion inhibitors [2]. However, there is an increasing need in the industry to limit the use of chemicals with severe human health and environmental impact, hence the search for greener alternatives by reformulating the existing products or by identifying new chemistries for developing safer products [3]. Several green scale inhibitors [4], demulsifiers [5], and corrosion inhibitors [6] have been reported in the literature. In this work, we are studying the corrosion protective abilities of two single component and green inhibitor compounds, chitosan and carboxymethyl cellulose (CMC) compared with a multiple-component and commercially available Cortron 1 inhibitor. The effects of temperature (25─60 °C), concentration of individual inhibitor (25─100 ppm) and the rotational speed of the working electrode (100 and 1500 rpm) will be evaluated against the corrosion protective abilities of all the inhibitor systems. However, if these simple and green single-component compounds could show remarkably high corrosion protection in CO₂ saturated saline solution for X60 pipeline steel compared to Cortron 1, they could serve as active components in corrosion inhibitor formulations with superior protection. Outside the present work, it is our goal to design such formulation with Chitosan and CMC with surface and bulk inhibition far better that Cortron against CO₂ corrosion inhibition in saline media for practical industrial applications.

**Experimental**

**2.1 Materials and equipment**

Cortron 1 and two green inhibitors, Chitosan and CMC, are employed in this study for low carbon (X60 grade) steel substrate typically used as oil pipeline material. A deoxygenated and CO₂ saturated 3.5 wt% NaCl solution was employed as the corrodenet. The electrochemical CO₂ induced corrosion experiments were conducted in a glass cell with a three electrode set-up, with platinum and saturated calomel electrode used as the counter and reference electrodes, respectively. Figure 1 displays a labeled schematic representation of the electrochemical glass cell set up for both dynamic and static experimental conditions with the electrolyte temperature controlled with a Benchtop Temperature Controller (US).
2.2 Electrochemical tests and surface analysis

The procedures for substrate pretreatment, CO₂ gas pre-saturation and electrochemical evaluations at static and dynamic experimental conditions has been reported elsewhere [7, 8, 9]. In this work, the performance of the inhibitors was evaluated at 1000 and 1500 rpm using Rotating Cylinder Electrode (RCE). The current RCE design allows for the mounting of specific shaped metal substrates in other to study their corrosion rates under high velocity (high shear, turbulent) flow conditions. The setup uses consists of three main components as reported in the literature [10], with the electrode (a conductive disk) embedded in an inert non-conductive polymer or resin that can be attached to an electric motor that has very fine control of the electrode's rotation rate.

Electrochemical Impedance Spectroscopy EIS experiments was performed under potentiostatic condition between 100 kHz to 100 mHz with a small amplitude perturbation (10 mV peak-to-peak) for an ac signal at E_{corr} using a Gamry Instrument potentiostat/galvanostat/ZRA (Ref 3000). The SEM-based surface analysis of X60 pipeline steel coupons after twenty four hours immersion in CO₂ saturated 3.5 wt% NaCl solutions in the absence and presence of the inhibitors was also investigated.

3.0 Result and discussions

3.1 Effect of inhibitor concentration

The effect of increment in the amount of the each inhibitor against the corrosion of X60 pipeline steel in 3.5% NaCl solution saturated with CO₂ was investigated using EIS method at 25°C. Figures 2 present the Nyquist curves in the presence and absence of varying concentrations of (a) Chitosan, (b) CMC and (c) Cortron with depressed full capacitive loops. The Nyquist plots for the three corrosion inhibitors are with similar curve shape indicative of an unchanged mechanism of protection as their concentrations inceased. Larger diameters of Nyquist semi-circles are attributes of
higher corrosion resistance systems of inhibitors compared to the blank solution, and in this study, higher concentrations of these inhibitors possess wider Nyquist curve widths showing dependence of concentration on the corrosion process. This electrochemical change is indicative of inhibition of corrosion process at increased concentration of the inhibitors by adsorbing on the surface of the metal thereby reducing the active surface area exposed to the aggressive corrosive electrolyte medium [11]. The reason for the relative distortions of the semi-circles could be attributed to the unevenness of the metal surface, and this phenomenon has been elaborately explained elsewhere [12].

Figure 2: EIS spectra for the effect of concentration of (a) Chitosan, (b) CMC and (c) Cortron as it affects X60 pipeline steel corrosion in CO₂ saturated 3.5% NaCl solution.

Table 1: EIS parameters for the effect of concentration of inhibitors as it affects X60 pipeline steel corrosion in CO₂ saturated saline (3.5% NaCl) solution.
Moreover, higher impedance values for the Nyquist curves obtained were recorded for the commercial corrosion inhibitor (Cortron) to two folds of a thousand compared to Chitosan and CMC. The reason for this varying superior resistance and protective performance in the presence of corrosive chloride ions and CO$_2$ could be due to the fact that Chitosan and CMC are single component substances which are relatively small water-soluble and linear polysaccharide compounds bearing simple amino and carboxymethyl groups, respectively, for less stronger metal surface interactions, while Cortron is an oil-based hybrid composite formulations consisting of active inhibitors, surfactant, enhancers, wetting agents and modifiers in methanol. Cortron 1 is a highly viscous suspension widely used in many complex oil-field based corrosion control and thus, remains a base-line protective pigment for the design and development of other field and lab-based inhibitor formulation. Chitosan and CMC were chosen to study comparatively with Cortron because of their unique electronic and molecular structures since their anticorrosive properties as compounds are largely linked with their chemical makeup (Figure 3). Distinctly, the β-(1-4)-linked D-glucosamine/ N-acetyl-D-glucosamine and carboxymethyl-bound glucopyranol moieties on chitosan and CMC, respectively, bear some O and N heteroatoms capable of adsorption at the surface of X60 steel thereby forming a mass/charge barrier against further corrosive attack, hence inhibition. Apart from being multifunctional group compounds, Chitosan and CMC are green, stable, benign and biodegradable inhibitors.

![Figure 3](image). Chemical structures of CMC and chitosan repeat unit.

![Figure 4](image). Equivalent circuit models used in fitting EIS experimental data for (a) blank and (b) inhibiting systems.
Equivalent circuit models provide an insight into the significance of the variation of impedance parameters from each response derived from the EIS spectra. The circuit model employed in fitting experimental data for the inhibiting system (Figure 4b) consists of $R_f$ and $\text{CPE}_1$ in parallel representing the adsorbed species forming films on the surface of X60 pipeline steel in the solution of the electrolyte with resistance ($R_s$); the charge transfer resistance ($R_{ct}$) and its double layer constant phase element component ($\text{CPE}_{dl}$) in parallel to the first set of components. $R_p$ calculated from Equation 1:

$$R_p = R_f + R_{ct}$$

The simple Randel circuit (Figure 4a) is employed in fitting the impedance data without the inhibitors (blank solutions). The derived electrochemical parameters from Nyquist plots (Figure 2a–d) for X60 pipeline steel in the CO$_2$ saturated 3.5% NaCl solution with and without different concentrations of Chitosan, CMC and Cortron are enlisted in Table 1. From the enlisted electrochemical data, the increase in the values of $R_f$ at the electrode/electrolyte interface is found to increase with the concentration of each inhibitor up to 100 ppm, except for cortron which is 75 ppm and then drops for the highest concentration. However, decrease in $R_f$ and $R_{ct}$ values for 100 ppm Cortron indicates a saturation of the adsorbed film at the electrode surface. At this concentration, the adsorbed species must have saturated the electrode surface and thus, become porous due to constant corrosive attack in the presence of the CO$_2$ gas. Again, the increase in the values of $R_f$ and $R_{ct}$ with concentration of the inhibitors confirms corrosion inhibition. Values of $R_{ct}$ for the three inhibitors are in this order: Cortron >> Chitosan > CMC; showing that the commercially available Cortron inhibitor formulation used in oilfields protects X60 pipeline steel better from sweet corrosion; this is comparable with Chitosan and CMC showing remarkably close protection abilities for X60 pipeline steel but are only single component water–soluble inhibitors. However, it is worthy to note here that there is no exact trend in the variation of $R_{ct}$ with the concentration of inhibitors. Similar erratic trend for resistances for each inhibitor concentration is observed for $\text{CPE}_{dl}$ (measured in µF/cm$^2$). Normally, decrease in values of CPE with concentration denotes a reduced extent of uptake of water at the metal surface (Equation 2); depicting an surface adsorption or reaction of molecules of the inhibitors at the metal surface with surrounding Fe$^{2+}$ ions thereby forming a $[\text{Fe} - \text{Inh}]^{2+}_{ads}$ type complex (Equations 3 and 4) [13].

$$\text{Inh}_{sol} + x\text{H}_2\text{O}_{ads} \rightarrow \text{Inh}_{ads} + x\text{H}_2\text{O}_{sol}$$  \hspace{1cm} (2)

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$$  \hspace{1cm} (3)

$$\text{Fe}^{2+} + \text{Inh}_{ads} \rightarrow [\text{Fe} - \text{Inh}]^{2+}_{ads}$$  \hspace{1cm} (4)

### 3.2 Effect of temperature

Apart from the concentration of inhibiting species in the corrosive medium, corrosion inhibiting process have been found to be dependent also on temperature. In this study, the effect of varying study temperature has been investigated in CO$_2$ saturated saline solution for X60 pipeline steel using ac electrochemical techniques in the presence of
100 ppm of each inhibitor conceived to give the highest inhibition efficiency in the previous test. Figure 5 presents EIS spectra in the presence and absence of 100 ppm Chitosan at varying process temperatures (25–60\(^\circ\) C). For every inhibitor in this study, a reduced corrosion protection was revealed for X60 pipeline steel in the CO\(_2\) saturated 3.5% NaCl solution as the temperature increase, evident in the decrease in the Nyquist semi-circle diameters.

**Figure 5**: EIS spectra for the effect of temperature as it affects X60 pipeline steel corrosion in CO\(_2\) saturated 3.5% NaCl solution in the presence and absence of 100 ppm (a) Chitosan, (b) CMC and (c) Cortron.

**Table 2**: EIS Parameters for the effect of temperature as it affects X60 pipeline steel corrosion in CO\(_2\) saturated saline (3.5% NaCl) solution in the presence and absence of Chitosan, CMC and Cortron.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Temp. ((^\circ)C)</th>
<th>CPE(_f) ((\mu)F/cm(^2))</th>
<th>(R_f) ((\Omega) cm(^2))</th>
<th>CPE(_{dl}) ((\mu)F/cm(^2))</th>
<th>(R_{ct}) ((\Omega) cm(^2))</th>
<th>(R_p) ((\Omega) cm(^2))</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>25</td>
<td>-</td>
<td>521</td>
<td>186.9</td>
<td>187</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>818</td>
<td>94.8</td>
<td>95</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>432</td>
<td>2175</td>
<td>24.6</td>
<td>47</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Chitosan</td>
<td>25</td>
<td>103</td>
<td>2175</td>
<td>24.6</td>
<td>47</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>98</td>
<td>1322</td>
<td>70.3</td>
<td>73</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>164</td>
<td>322</td>
<td>322</td>
<td>304</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>CMC</td>
<td>25</td>
<td>266</td>
<td>322</td>
<td>272.0</td>
<td>304</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>439</td>
<td>3950</td>
<td>0.0</td>
<td>111</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>178</td>
<td>1045</td>
<td>82.0</td>
<td>90</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>Cortron</td>
<td>25</td>
<td>4</td>
<td>281</td>
<td>1601.0</td>
<td>1610</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>455</td>
<td>434.1</td>
<td>445</td>
<td>79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3</td>
<td>466</td>
<td>376.8</td>
<td>379</td>
<td>87</td>
<td></td>
</tr>
</tbody>
</table>
Smaller semi-circle diameters representing higher corrosion rates for steel are revealed at $60^\circ$ C than the lower temperatures for all the inhibitors. Appropriate equivalent circuit models were used in fitting the impedance data and to provide an insight into the significance of temperature variation with corrosion inhibition. The derived electrochemical parameters from Nyquist plots for each inhibitor system after fitting the EIS data with these models in Figure 2e between 25-60$^\circ$ C are displayed in Table 2. From the Table 2, derived values of $R_l$ and $R_{ct}$ decrease at the electrode/electrolyte interface as the temperature increases revealing increased corrosion rate for X60 pipeline steel in CO$_2$ saturated saline solution in the absence and presence of the corrosion inhibitors. Compared to CMC, chitosan still retains higher values of $R_{ct}$ showing superior protection for X60 steel. The trend of charge transfer resistance values indicates that Chitosan and CMC competed favorably with remarkable protection compared to Cortron a hybrid composite of many anticorrosive additives at this temperature.

Generally, increase in corrosion resistance of metals in the presence of inhibitors at higher temperatures can be attributed to desorption of the inhibitor molecules from the metal surface. This phenomenon is suggestive of physical adsorption being that molecules of the inhibitor displaced of adsorbed water molecules and attached to the metal surface without chemical bonding (via van der waal forces) [7,12]. However, high temperature favors the formation of layers of FeCO$_3$ on the electrode surface that further aids the protection of the substrate (Equation 5); this can be observed in the trend of %IE. Adsorption of the molecules of the inhibitors tends to reduce the X60 steel corrosion at 25$^\circ$ C; but at 40$^\circ$ C, the %IE values drops due to molecular desorption and then rises again, subsequently, at 60 $^\circ$C. The percentage increase in the magnitude of %IE between 40 and 60 $^\circ$C for Chitosan, CMC, and Cortron were 89, 68 and 9%, respectively. The reason for this increment in the values of the corrosion inhibition efficiency at 60$^\circ$ C is due to the formation of FeCO$_3$ precipitate and a [FeCO$_3$-Inh] type complex, thereby further protecting the steel surface.

$$Fe^{+2} + CO_3^{-2} \rightarrow FeCO_3$$

### 3.3 Effect of rotational speed

Most corrosion inhibition studies for metal corrosion are centered on static conditions with the search for the optimal concentration to which a particular compound or group of compounds can inhibit corrosion in a particular medium [8]. Static conditions are limited in nature and the few researches have studied the effect of flow conditions as it affects the rate of formation of protective films at the metal/electrolyte interface relative to the speed of working electrode rotation [14]. In this study, the inhibitive performance of Chitosan, CMC and Cortron for X60 pipeline metal in the CO$_2$ saturated saline solution under dynamic conditions was also investigated at 1000 and 1500 rpm using a rotating cylinder electrode (at 25$^\circ$ C) with the setup in Figure 1.
Table 3: EIS parameters for the effect of rotational speed as it affects X60 pipeline steel corrosion in CO\textsubscript{2} saturated saline (3.5% NaCl) solution in the presence and absence of Chitosan, CMC and Cortron.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Rotational Speed (rpm)</th>
<th>CPE\textsubscript{f}</th>
<th>R\textsubscript{f}</th>
<th>CPE\textsubscript{dl}</th>
<th>R\textsubscript{ct}</th>
<th>R\textsubscript{p}</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1000</td>
<td>-</td>
<td>-</td>
<td>1262</td>
<td>129.0</td>
<td>129</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>-</td>
<td>-</td>
<td>1602</td>
<td>82.2</td>
<td>82</td>
<td>-</td>
</tr>
<tr>
<td>Chitosan</td>
<td>1000</td>
<td>796</td>
<td>3.5</td>
<td>1783</td>
<td>73.9</td>
<td>77</td>
<td>-67</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>547</td>
<td>2.0</td>
<td>2575</td>
<td>68.6</td>
<td>71</td>
<td>-16</td>
</tr>
<tr>
<td>CMC</td>
<td>1000</td>
<td>220</td>
<td>1.6</td>
<td>1776</td>
<td>108.6</td>
<td>110</td>
<td>-17</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>163</td>
<td>1.1</td>
<td>1672</td>
<td>123.5</td>
<td>125</td>
<td>34</td>
</tr>
<tr>
<td>Cortron</td>
<td>1000</td>
<td>4</td>
<td>66.3</td>
<td>496</td>
<td>699.9</td>
<td>766</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>3</td>
<td>65.0</td>
<td>238</td>
<td>951.0</td>
<td>1016</td>
<td>92</td>
</tr>
</tbody>
</table>

Figures 6 present the impedance spectra in the presence and absence of different concentrations of (a) Chitosan, (b) CMC and (c) Cortron, respectively. The shapes of the Nyquist curves are similar an indication of an unchanged mechanism of metal dissolution in the corrosive medium in the absence and presence of inhibitors as the speed of the rotating cylinder electrode (RCE) changes. Generally, in uninhibited solutions, the corrosion rate of metal substrates should be increase with increasing rotational speed [8]; this has been affirmed for X60 pipeline metal in the blank CO\textsubscript{2} saturated saline solution. Increase in the diameter of the Nyquist plots are observed for blank solution at 1000 rpm compared to 1500 rpm. However, in the presence of inhibitor, increase in rotational speed implies that more inhibitor molecules reached the metal surface to formed protective film, thereby improving corrosion inhibition. At low
rotational speed, reduced mass transport of the inhibitor molecules around the metal surface in turn reduces the shear stress thereby separating the layers of adsorbed protective films at the metal/electrolyte interface; hence inhibition reduction [8, 9]. In the present study, corrosion inhibition efficiency is found to increase with increase in the rotational speed for Cortron and CMC. Table 3 presents the derived electrochemical parameters after fitting the impedance data with appropriate equivalent circuit models for X60 pipeline steel in the CO₂ saturated 3.5% NaCl solution in the absence and presence of 100 ppm Chitosan, CMC and Cortron at 1000 and 1500 rpm. From the electrochemical data on Table 3, the gradual decrease in CPEₐ values with increased rotational speed for each inhibitor system provides evidence of corrosion inhibition at higher speed of rotation. Higher CPEₐ values are obtained in the absence of the inhibitors with magnitude of 1262 and 1602 µF/cm² recorded at 1000 and 1500 rpm, respectively, for the blank solution. As expected for Rₜ at higher rotational speed, increased Rₜ values are recorded for 1500 rpm for only CMC and Cortron; and the reason for the erratic electrochemical behavior for Chitosan is not entirely clear. At this rotational speed, 82.2 Ω cm², being the least Rₜ value in this study, is recorded for the blank CO₂ saturated 3.5% NaCl solution. Trend in Rₜ values therefore proves that for the blank uninhibited solutions, the rate of metal substrate dissolution increases with rotational speed [8]. However, the enhanced corrosion rate observed for CMC suggests that no protective inhibitor adsorbed film was formed. The trend in IE values suggests that CMC is a better corrosion inhibitor for X60 pipeline steel in dynamic condition. Negative of values of %IE denote non-inhibition for a corrosion inhibitor at that rotational speed.

3.4 Surface analysis

Surface morphological examinations of the exposed steel specimens in uninhibited CO₂ saturated saline and inhibited solutions containing pure biopolymers as corrosion inhibitor compounds and commercially-available corrosion inhibitor (Cortron) were evaluated using SEM. Figure 7 shows SEM images of the exposed X60 steel in CO₂ saturated saline solution in the (a) absence and presence of 100 ppm Chitosan (b) and (c) CMC compared with Cortron (d) at room temperature after 24 hr immersion.
The steel substrate in the uninhibited blank solution shows severe corrosion on the surface with huge corrosion product mass due to uncontrolled dissolution as well as the other degradation episodes caused by the presence of carbonic acid in the solution of the electrolyte (Figure 7a). While the steel substrate shows relatively uniform corrosion in the presence of Chitosan, there seems to be evidence of localized attack for the coupon in 100 ppm CMC in the solution of the electrolyte. Generally, the presence of all the corrosion inhibitors shows visible reduction in corrosion of X60 pipeline steel to a great extent due adsorption of molecules and subsequent formation of protective layers on the metal surface [11, 14]. Cortron continues to show superior corrosion protection. This is evident in the clear SEM micrograph of the steel coupon in the solution of the electrolyte containing this inhibitor formulation — with few mold-like corrosion products and scales as continuous surface features.

3.5 Adsorption isotherm

Corrosion inhibition is due to the direct adsorption of molecules of the inhibitors on the metal surface and/or could also involve the reaction of these compounds with a secondary compound to generate a film capable of forming a layer of protection at the metal/electrolyte interface. These surface adsorption process can be approximated by isotherm models using the magnitude of the surface coverage ($\theta$) for a particular range of inhibitor concentration [15]. In the current work, the adsorption of Chitosan and CMC and Cortron on the surface of the X60 pipeline steel substrate has been approximated using Langmuir adsorption isotherm (mathematically expressed in Equation 6) and presented in Figure 8 for the range of concentration of the inhibitors under study at 25°C.

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

(6);

where inhibitor concentration ($C$) is measure in ppm; inhibitor’s surface coverage is denoted as $\theta$ and the $K_{ads}$ is the equilibrium constant associated with interfacial molecular adsorption.
Table 4: Langmuir adsorption parameters for the inhibitor adsorption on X60 pipeline steel.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$\Delta G^0_{ads}$ (KJ/mol)</th>
<th>$K_{ads}$</th>
<th>Slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>25.14</td>
<td>0.0255</td>
<td>2.29</td>
<td>0.97</td>
</tr>
<tr>
<td>CMC</td>
<td>23.03</td>
<td>0.0109</td>
<td>1.45</td>
<td>0.92</td>
</tr>
<tr>
<td>Cortron</td>
<td>35.28</td>
<td>1.5300</td>
<td>1.11</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The linear regression ($R^2$) values were used to ascertain how much the experimental impedance data fits the model — though $R^2 > 0.9$ is recorded (Figure 6(B)), thus indicative of a good fit though the gradients of curves are $> 1$. Non-unity slopes of Langmuir adsorption isotherm usually expresses inconsistency of experimental adsorption data with monolayer adsorption pattern proposed in the model. Langmuir adsorption isotherm also postulates unequivalence inhibitor adsorption sites of surfaces as well as the independency in molecular adsorption with number of available sites [16, 17]. The magnitude of $K_{ads}$ in Equation 7 is empirically related to standard Gibbs energy ($\Delta G_{ads}$) of adsorption by Equation 4.13.

$$\Delta G_{ads}^0 = -RT \ln(1 \times 10^6 K_{ads}) \quad (7)$$
where the absolute temperature, $T$ is measured in $K$; the molar gas constant, $R$, is expressed in J/K/mol and the magnitude of the concentration of water molecules, $1 \times 10^{-6}$, is expressed in ppm. The calculated values of $K_{ads}$ (constant of adsorption–desorption process) are 0.0255, 0.0109 and 1.53, respectively, for chitosan, CMC and Cortron with $-25.2$, $-23.0$ and $-35.3$ J/mol being the designated magnitudes of $\Delta G_{ads}$ for the inhibitors (Table 4). The range of $\Delta G_{ads}$ are suggestive of a non-electrostatic metal-inhibitor interaction, proving that molecules of the inhibitors must have been adsorbed on the surface of the steel substrate by mixed physical adsorption and actual chemical reaction to which new chemical bonds were generated. The negative magnitude of $\Delta G_{ads}$ is indicative of thermodynamic spontaneity associated with the adsorption process of the inhibitors onto the X60 pipeline steel surface.

4. Conclusions

Two single component compounds, Chitosan and CMC, have been found to inhibit X60 pipeline steel corrosion in CO$_2$ saturated saline solution to some extent compared to Cortron, a typical multi-component inhibitor formulation used in the oil-field. The corrosion inhibition efficiency was found to be dependent on the concentration of the individual inhibitor; the rotational speed of the working electrode and the immersion period. Increased rotational speed (1500 rpm) enhanced the migration of more inhibitor molecules by mass transfer to the metal surface to formed protective film, thereby improving corrosion inhibition. Adsorption of molecules of the inhibitor molecules on the surface of the X60 pipeline steel substrate has been approximated by Langmuir adsorption isotherm, and corrosion inhibition has been described in terms of assumptions of this model. The charge-transfer process and associated double-layer behavior of the metal/solution interface has been described to be related to the high-frequency capacitive loop of impedance spectra. Equivalent circuit models provided an insight into the significance of the variation of impedance parameters from each response derived from the EIS spectra. Low concentrations of these single-component inhibitor compounds reduced corrosion redox reactions and corrosion current densities, but enhanced impedance and total ($R_i$ and $R_{ct}$) resistances. SEM studies of the surface of the steel substrate in the solution of the electrolyte containing these inhibitors showed improved protection due to formation of anticorrosive films. X60 coupon surfaces revealed more uniform and smoother surfaces. With a remarkable protection for steel in CO$_2$ saturated saline solution at a concentration as low as 100 ppm for Chitosan and CMC, these single–component inhibitor compounds could under appropriate formulation serve as anticorrosive additives for low carbon steel corrosion in CO$_2$-saturated NaCl environment as Cortron commercial inhibitor with practical industrial applications.

References


