2-Butyne-1,4-diol as a novel corrosion inhibitor for API X65 steel pipeline in carbonate/bicarbonate solution

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ABSTRACT

The inhibition effects of 2-butyne-1,4-diol on the corrosion susceptibility of grade API 5L X65 steel pipeline in 2 M Na2CO3/1 M NaHCO3 solution were studied by electrochemical techniques and weight loss measurements. The results indicated that this inhibitor was a mixed-type inhibitor, with a maximum percentage inhibition efficiency of approximately 92% in the presence of 5 mM inhibitor. Atomic force microscopy revealed that a protective film was formed on the surface of the inhibited sample. The adsorption of the inhibitor was found to conform to the Langmuir isotherm with the standard adsorption free energy of −21.08 kJ mol−1.

1. Introduction

Steel pipelines play an important role in transporting gases and liquids throughout the world [1]. Corrosion is a serious problem in steel pipelines because replacing, repairing and maintaining them can be extremely expensive and time-consuming [1–5]. The water content accompanying the oil production process has been found to be a significant factor in the internal corrosion of steel pipelines because the water contains many corrosive agents such as carbon dioxide, hydrogen sulphides, organic acids and salts [6–14]. Cathodic protection reactions are the most common examples of aggressive corrosion processes in terms of external pipeline surfaces in soils [5,13,15–17]. For instance, these chemical reactions create considerable concentrations of carbonate/bicarbonate ions in the soil environment [5,18–22].

For many years, the application of corrosion inhibitors, such as organic inhibitors, has been the most common method for controlling (reducing) the corrosion of steel pipelines in acidic and alkaline environments [23–27]. In aqueous alkaline systems, the presence of certain ions such as carbonate/bicarbonate ions tends to oppose the action of inhibitors.

Corrosion protection by organic inhibitors is mostly based on modification of the metal surface through the adsorption of inhibitor molecules and the subsequent formation of a protective blocking layer [2,28–34]. These compounds are often simultaneously affected by both anodic and cathodic corrosion reactions; therefore, they are sometimes referred to as mixed-type corrosion inhibitors [28–34]. Acetylenic compounds are known as strong organic corrosion inhibitors in acid solutions [35], but less effort has been directed toward investigating these inhibitors in alkaline solutions [36,37].

In general, it has been found that in alkaline solutions, the concentration of the dissolved salts has considerable influence on the performance of inhibitors and that the concentration of the inhibitor required for protection depends on the concentration of these aggressive species [38].

Two important acetylenic alcohols are 2-butyne-1,4-diol (C4H6O2) and propargyl alcohol (C3H4O), which have been examined using different techniques [33]. It is generally accepted that the triple bonds of acetylenic alcohols are an important factor in corrosion inhibition because of the p-electron interactions [39–41]. Recently, the inhibitive properties of 2-butyne-1,4-diol on mild steel in sulphuric acid solutions were investigated [33]. The results indicated that the introduction of 2-butyne-1,4-diol into sulphuric acid solution can lead to the formation of a thin inhibitor film on the steel surface, which causes a decrease in the surface roughness and effectively protects the steel from corrosion. Other studies have also revealed that inhibition efficiency increases upon increasing the inhibitor concentration. Potentiometric studies have shown that these inhibitors act as a mixed-type inhibitor, and the inhibition efficiency of these additives increases upon increasing the size of the acetylenic chain [33,34,42].

The objective of this study was to examine the inhibition performance of the acetylenic alcohol 2-butyne-1,4-diol and its influence on the corrosion behaviour of API X65 steel pipeline in 2 M Na2CO3/
1 M NaHCO₃ solution as well as to identify the adsorption isotherm that describes the behaviour of this inhibitor molecule on the steel pipeline surface. The effects of exposure time, inhibitor concentration and solution temperature on inhibitor performance were studied.

2. Materials and methods

2.1. Specimen

Tests were performed on a pipeline steel of the following chemical composition (wt.%): 0.07% C, 0.24% Si, 1.35% Mn, 0.017% P, 0.005% S, 0.16% Cr, 0.18% Ni, 0.12% Mo, 0.01% Cu and the remainder Fe.

This material was made according to API 5L grade X65 specifications and had a ferrite–pearlite microstructure, as shown in Fig. 1. The nominal pipe wall thickness was 1.9 mm. The yield strength of the pipe section and the ultimate tensile strength were measured to be 526 and 648 MPa, respectively, with an elongation at failure of 17%.

The specimens used in electrochemical measurements were mechanically cut into 1.0 × 1.0 × 0.5 cm dimensions, abraded by a series of emery papers (up to grade 2500) and mechanically polished to a mirror finish using aqueous alumina suspensions (with particle sizes decreasing down to 0.05 μm). Prior to each measurement, the specimen was ultrasonically cleaned for 3 min in an ethanol bath and rinsed with distilled water. Finally, the metal plate was thoroughly rinsed with distilled water.

2.2. Solution preparation

Experiments were done in stagnant 2 M Na₂CO₃/1 M NaHCO₃ solution in the absence and presence of different concentrations of 2-butyne-1,4-diol as a corrosion inhibitor. The molecular structure of 2-butyne-1,4-diol is shown in Fig. 2. All purchased chemicals of 2-butyne-1,4-diol as a corrosion inhibitor. The molecular structure of 2-butyne-1,4-diol is shown in Fig. 2. All purchased chemicals were of reagent grade (Merck) and were used without further purification.

Fresh solution and fresh steel samples were used after each immersion. The cleaned samples were weighed before and after immersion of the specimen into the corrosive solution and without bubbling. The submersion lasted for 3 h at a solution temperature of 25 °C, with the temperature being controlled by an aqueous thermostatted bath. The specimens were washed with distilled water and acetone, and then they were dried at room temperature. Then, an analytical balance (precision of ±0.1 mg) was used to determine the weight loss, and the mean weight loss and corresponding standard deviation were calculated.

2.4. Potentiodynamic polarization and EIS measurements

Electrochemical experiments (potentiodynamic polarization and the EIS) were performed in a conventional three-electrode cell in which a saturated calomel electrode (SCE) was the reference electrode, platinum foil was the counter electrode and the API X65 steel was the working electrode (WE). All potentials quoted in this paper were referred to the SCE. The area of the WE exposed to the solution was 0.196 cm².

Before electrochemical measurement the specimens were immersed in test solution at open circuit potential (Eoc) for 1 h to be sufficient to attain a stable state. The polarization curve was acquired by scanning the potential range between +200 and +1400 mV (vs. OCP) using a computer-controlled potentiostat/galvanostat (EG&G Princeton Applied Research A273) at a scanning rate of 0.6 mV s⁻¹. EIS measurements were carried out using EG&G A273 with an AC amplitude of the sinusoidal perturbation of 10 mV and measurement frequency from 10 down to 100 kHz at the OCP. The computer system was equipped with a PowerSuite software analyser to record EIS data and the Zview program to determine the values of the parameters of the proposed electric circuit model. Moreover, the impedance data were fitted and the pertinent EIS parameters were extracted using the Zview program.

Fresh solution and fresh steel samples were used after each sweep. For each experimental condition, two to three measurements were performed to ensure the reliability and reproducibility of the data.

2.5. Characterization of surface films

The morphology of the corroded surface of each specimen and film formed on the steel surface were examined by Philips XL30 scanning electron microscopy. The specimens were washed and dried after being withdrawn from the test cell to enable the characterization of adherent corrosion products with no salt residues.

2.6. AFM studies

The topographic changes of the corroded surface of each specimen were monitored in standard mode with a commercial AFM instrument from Molecular Image (Pico Scan). Micro-fabricated Si₃N₄ pyramidal cantilevers (120 μm in length) with integrated Si₃N₄ tips (20–50 nm radius of curvature) were used. The average constant of the cantilevers was 0.58 Nm⁻¹ and the typical force during the measurements was less than 1 nm. First, the samples were abraded with SiC abrasive paper up to 4000 grade, followed by washing with distilled water and acetone. After different immersion times in 2 M Na₂CO₃/1 M NaHCO₃ solution with and without inhibitor at room temperature, the specimens were cleaned with distilled water and acetone, dried with a cold air blaster, and then submitted to atomic force microscopy examinations.
3. Results and discussion

3.1. Weight loss measurements

The weight loss method is beneficial for monitoring inhibition efficiency because of its simple usage and reliability [44]. For the present study, the reproducibility of the weight loss and inhibition efficiency values for triplicate determinations were very accurate (±5%). Fig. 3 shows the weight loss data and the percentage inhibition efficiencies ($\eta_w$ %) in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution at various concentrations of 2-butyne-1,4-diol and for different immersion times. The percentage inhibition efficiency ($\eta_w$ %) and surface coverage ($\theta$) were determined by the following equations:

$$\eta_w(\%) = \frac{W_0 - W_1}{W_0} \times 100$$

$$\theta = \frac{W_0 - W_1}{W_0}$$

where $W_0$ and $W_1$ are the values of the steel corrosion rate with and without the inhibitor, respectively. Gravimetric measurements showed that the corrosion rate decreased in the presence of 2-butyne-1,4-diol, the inhibition efficiency ($\eta_w$) increased with the 2-butyne-1,4-diol concentration and the surface coverage defined by $\theta$ reached a maximum of 0.925 at 5 mM. The inhibition can be explained by the adsorption of 2-butyne-1,4-diol [33]. Fig. 3 also shows variations of the inhibition efficiency as a function of the immersion time and concentration of the inhibitor. The inhibition increased with an increase of the immersion time and stabilised at a value of 0.925 after 3 h. Furthermore, increasing the immersion time from 3 to 6 h caused a noticeable decrease in the inhibition efficiency. This is due to the considerable inhibition efficiencies that can be realized using symmetrical acetylenic compounds. The adsorption coverage of inhibitor on the steel surface increases with the inhibitor concentration.

3.2. Potentiodynamic measurements

The potentiodynamic polarization parameters in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution with and without various concentrations of 2-butyne-1,4-diol at 25 °C are listed in Table 1. These parameters include the values of corrosion current densities ($I_{corr}$), corrosion potential ($E_{corr}$), cathodic Tafel slope ($b_c$), anodic Tafel slope ($b_a$) and inhibition efficiency ($\eta_p$). Both cathodic and anodic reactions were suppressed by the addition of 2-butyne-1,4-diol (Fig. 4), which suggests that 2-butyne-1,4-diol reduces anodic dissolution and retards the hydrogen evolution reaction. In other words, the presence of 2-butyne-1,4-diol causes a prominent decrease in the corrosion rate, i.e., shifts both the anodic and cathodic curves to lower current densities. Moreover, both the cathodic and anodic reactions of steel corrosion were drastically retarded by 2-butyne-1,4-diol in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$. Clearly, $I_{corr}$ was remarkably decreased, while $\eta_p$ increased with the inhibitor concentration and the maximum $\eta_p$ was 0.92 at 5 mM 2-butyne-1,4-diol. There was no definite trend in the shift of $E_{corr}$ in the presence of 2-butyne-1,4-diol; therefore, 2-butyne-1,4-diol could be a mixed-type inhibitor, with the inhibitory action caused by a geometric blocking effect [44]. In addition, the inhibitory action was
Table 1
Potentiodynamic polarization parameters for the corrosion of steel pipeline samples in 2 M Na₂CO₃/1 M NaHCO₃ containing different concentrations of 2-butyne-1,4-diol at 25 °C.

<table>
<thead>
<tr>
<th>Concentration of inhibitor (mM)</th>
<th>Icorr (μA cm⁻²)</th>
<th>Ecorr (mV vs. SCE)</th>
<th>b₁ (mV dec⁻¹)</th>
<th>b₂ (mV dec⁻¹)</th>
<th>Corrosion rate (mg cm⁻² day⁻¹)</th>
<th>ηp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>3.686</td>
<td>-330</td>
<td>317</td>
<td>569</td>
<td>1.447</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>0.995</td>
<td>-305</td>
<td>142</td>
<td>341</td>
<td>0.389</td>
<td>0.73</td>
</tr>
<tr>
<td>2.5</td>
<td>0.516</td>
<td>-289</td>
<td>133</td>
<td>369</td>
<td>0.203</td>
<td>0.86</td>
</tr>
<tr>
<td>5.0</td>
<td>0.295</td>
<td>-276</td>
<td>109</td>
<td>261</td>
<td>0.116</td>
<td>0.92</td>
</tr>
<tr>
<td>10.0</td>
<td>0.332</td>
<td>-264</td>
<td>82</td>
<td>195</td>
<td>0.130</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Fig. 4. Potentiodynamic polarization curves for the steel samples in 2 M Na₂CO₃/1 M NaHCO₃ solution containing different concentrations of 2-butyne-1,4-diol at 25 °C (the immersion time was 3 h).

due to a reduction of the reaction area on the surface of the corroding metal [45]. The inhibition efficiency (ηp) was calculated by the following equations:

\[
\eta_p = \frac{I_{corr(0)} - I_{corr(inh)}}{I_{corr(0)}}
\]

(3)

where \(I_{corr(0)}\) and \(I_{corr(inh)}\) are the corrosion current densities without and with the inhibitor, respectively. The anodic and cathodic Tafel slopes significantly changed in the presence of 2-butyne-1,4-diol, which may have been due to carbonate ions or inhibitor molecules adsorbed on the steel surface (Fig. 4). The behaviour indicated that 2-butyne-1,4-diol acts as a mixed-type inhibitor, affecting both the anodic and cathodic reaction mechanisms. For 2-butyne-1,4-diol, not only the Tafel slope, but also the corrosion potential was considerably changed when compared with that of the blank. It was evident from Table 1 that upon increasing the inhibitor concentration to 5 mM, corrosion current density values significantly decreased and the inhibition efficiency increased; however, a further increase in inhibitor concentration to 10 mM decreased the inhibition efficiency. This is likely because adsorptive and protective films of the inhibitor molecules were formed on the steel surface. The film acted as a physical barrier to restrict the diffusion of corrosive species to the steel surface. Additionally, the anodic slope increased, which may have been due to the formation of a protective film. It is worth noting that this effect is dependent on the surface conditions. When the specimens were pre-corroded, the anodic slopes were higher than when non-pre-corroded specimens were immersed in an inhibitor solution. This could be related to interactions between the corrosion products, inhibitor adsorption and film formation. Changes in the cathodic slopes were also correlated to the surface conditions. Thus, it seems that longer periods of pre-corrosion testing are required to fully understand the behaviour [46].

For 2-butyne-1,4-diol, the corrosion current density decreased and the inhibition efficiency increased upon increasing the inhibitor concentration. The highest inhibition efficiency was 0.92 at 5 mM. The inhibition efficiency increased with an increase in the surface coverage (θ). The high inhibition efficiency was due to bonding of the adsorbed film on the steel surface [24]. The inhibition efficiencies were in good agreement with those calculated from the weight loss measurements.

3.3. Electrochemical impedance spectroscopy

3.3.1. Effect of the inhibitor concentration on inhibitor performance

Fig. 5 presents Nyquist diagrams of the steel measured in 2 M Na₂CO₃/1 M NaHCO₃ with and without various concentrations of 2-butyne-1,4-diol at 25 °C. It should be noted that if the adsorption of inhibitors had a considerable influence on the interface, both the ratio of time constants and characterization of the adsorption process must change. The Nyquist plots consisted of two capacitive loops. The one at high frequency (in the right part of the figure) was related to charge transfer resistance, which could correlate to resistance between the steel and outer helmholtz plane [47]. Conversely, the one at low frequency (in the left part of the figure) was attributed to the adsorbed film resistance due to adsorption of the inhibitor and all other accumulated products [47]. Deviations from a perfect circular shape (depression) are often related to the frequency dispersion of interfacial impedance arising from a lack of homogeneity of the electrode surface due to roughness or interfacial phenomena [48].

The EIS results were simulated using the equivalent circuit shown in Fig. 6 in relation to pure electric models, which can verify...
Table 2

<table>
<thead>
<tr>
<th>Concentration of the inhibitor (mM)</th>
<th>$C_{dl}$ (μF cm$^{-2}$)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_p$ (Ω cm$^2$)</th>
<th>CPE (μF cm$^{-2}$)</th>
<th>$\eta$</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>5092</td>
<td>5.559</td>
<td>23.70</td>
<td>934</td>
<td>0.85</td>
<td>38</td>
<td>0.85</td>
</tr>
<tr>
<td>1.0</td>
<td>1476</td>
<td>5.223</td>
<td>82.03</td>
<td>270</td>
<td>0.86</td>
<td>131</td>
<td>0.710</td>
</tr>
<tr>
<td>2.5</td>
<td>814</td>
<td>5.374</td>
<td>148.70</td>
<td>150</td>
<td>0.87</td>
<td>237</td>
<td>0.840</td>
</tr>
<tr>
<td>5.0</td>
<td>387</td>
<td>5.608</td>
<td>313.01</td>
<td>71</td>
<td>0.87</td>
<td>500</td>
<td>0.924</td>
</tr>
<tr>
<td>10.0</td>
<td>509</td>
<td>4.228</td>
<td>237.90</td>
<td>93</td>
<td>0.88</td>
<td>380</td>
<td>0.900</td>
</tr>
</tbody>
</table>

where $f_{\text{max}}$ represents the frequency at which the imaginary value reaches a maximum on the Nyquist plot. According to the above-mentioned equivalent circuits, the experimental data were fitted very well and the impedance diagrams for 2-butyne-1,4-diol could be described well using the model presented in Fig. 6. The percentage inhibition efficiency was calculated by the following equations:

$$\eta(\%) = \frac{R_{ct(0)} - R_{ct(\text{inh})}}{R_{ct(0)}} \times 100$$

where $R_{ct(0)}$ and $R_{ct(\text{inh})}$ are values of the charge transfer resistance observed in the absence and presence of 2-butyne-1,4-diol. The EIS parameters are also summarized in Table 2. The electrochemical parameters of $R_s$, $C_{dl}$ and $\eta$ were calculated with the Zview software and are presented in Table 2. Based on Table 2, the $R_s$ values were prominently increased while the $C_{dl}$ values declined with the concentration of 2-butyne-1,4-diol. Theoretically, the decrease in $C_{dl}$ was comparable to that in the blank solution, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that inhibitor molecules function through adsorption at the metal/solution interface [24]. The impedance spectra consisted of small capacitive loops at high frequencies followed by a large loop at low frequency values. The high frequency capacitive loop was related to charge transfer of the corrosion process and the double layer behaviour. In addition, the low frequency inductive loop may have been due to the relaxation process of adsorbed species, such as inhibitor species [52], on the electrode surface. It may also have been due to re-dissolution of the passivated surface at low frequencies [52]. These high frequency loops were not perfect semicircles, which could be attributed to frequency dispersion because of the roughness and heterogeneousness of the electrode surface [53]. Furthermore, the diameter of the capacitive loop in the presence of inhibitor increased with the inhibitor concentration and was larger than that in the absence of inhibitor (blank solution). This behaviour indicated that impedance of the inhibited substrate increased upon increasing the inhibitor concentration. Table 2 shows that the capacitance values decreased and the charge transfer resistance increased upon increasing the inhibitor concentration, and the obtained $\eta$ values were in good agreement with those determined from the polarization curves.

The inhibition efficiency increased with the concentration of 2-butyne-1,4-diol and the maximum inhibition efficiency was 0.924, which further confirmed that 2-butyne-1,4-diol exhibits very good inhibitive performance for steel in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$. The inhibition efficiencies obtained from weight loss measurements ($\eta_w$), potentiodynamic polarization curves ($\eta_p$) and EIS ($\eta$) were in reasonable agreement. A comparison of the $\eta$ values (Table 3) obtained using these three methods also showed acceptable agreement. This agreement among these independent techniques proves the validity of the results.

3.3.2. The effects of immersion time on the inhibitor performance

To investigate the 2-butyne-1,4-diol adsorption kinetics and determine the time needed for 2-butyne-1,4-diol to reach its maximum inhibition efficiency, EIS experiments were carried out in the presence of 5 mM 2-butyne-1,4-diol in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ at different immersion times at 25 °C (Fig. 7). A comparison of the results of $R_s$ with 5 mM 2-butyne-1,4-diol at different immersion times is presented in Table 4. $R_s$ increased upon increasing the immersion time up to 3 h and then became relatively constant. From the figure, $R_s$ slightly increased upon increasing the inhibitor concentration at a given immersion time. This may indicate that the inhibitor film becomes slightly more effective at higher inhibitor concentrations. Increasing the inhibitor concentration may not yield good performance of the inhibitor film for longer immersion times. The decrease in $C_{dl}$ values was caused by an imperceptible replacement of water molecules due to the adsorption of inhibitor molecules on the steel surface, decreasing the extent of the dissolution reaction [54,55]. The corresponding corrosion resistance and corrosion inhibition efficiency values were calculated and are presented in Table 4. The data demonstrated that even 3 h after adding 2-butyne-1,4-diol to the electrolyte, the corrosion inhibition efficiency reached 0.924. The AC impedance study also corroborated the inhibitory character of 2-butyne-1,4-diol obtained based on polarization curves. Inhibitors usually act at a solid surface by forming an adsorbed film or by inducing the formation a layer of corrosion products. The adsorption depends on the charge of the metallic surface, the charge or dipole moment of the inhibitor molecule and the adsorption of other ionic species present in solution [56].

3.3.3. The effects of solution temperature on inhibitor performance

The influence of temperature on the corrosion inhibition efficiency of 2-butyne-1,4-diol was studied in a temperature interval...
Table 3
Inhibition efficiency values obtained from weight loss, potentiodynamic polarization and electrochemical impedance measurements of steel in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution containing various concentrations of 2-butyne-1,4-diol at 25 °C (the immersion time was 3 h).

<table>
<thead>
<tr>
<th>Concentration of the inhibitor (mM)</th>
<th>Inhibition efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
</tr>
<tr>
<td>1.0</td>
<td>0.796</td>
</tr>
<tr>
<td>2.5</td>
<td>0.841</td>
</tr>
<tr>
<td>5.0</td>
<td>0.925</td>
</tr>
<tr>
<td>10.0</td>
<td>0.921</td>
</tr>
</tbody>
</table>

Fig. 7. Nyquist plots of the corrosion of steel in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution at different immersion times at 25 °C (the concentration of 2-butyne-1,4-diol was 5 mM).

from 25 to 50 °C in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution. Fig. 8 shows the corresponding results of the corrosion inhibition efficiency calculated using EIS measurements. It was found that with increasing temperature, the steel corrosion resistance decreased in both the presence and absence of 2-butyne-1,4-diol, which was expected. However, the decreasing trend in the corresponding corrosion inhibition efficiency (Table 5) indicated that the relative steel corrosion resistance in the presence of 2-butyne-1,4-diol was more temperature-dependent than that in the absence of 2-butyne-1,4-diol. This could be explained on the basis of temperature-dependent 2-butyne-1,4-diol adsorption/desorption processes. For example, with an increase in temperature, the 2-butyne-1,4-diol adsorption equilibrium could shift towards the desorption process, resulting in a lower surface coverage [37]. This would also result in a decrease in 2-butyne-1,4-diol surface conformation order and, thus, decrease the protection against corrosive ions. Nevertheless, the corrosion inhibition efficiency was relatively high, even at 50 °C. Noor et al. [57] suggested that with an increase in temperature, some chemical changes occur in the inhibitor molecules, leading to an increase in the electron density at the adsorption centres of the molecule, which causes an improvement in inhibition efficiency.

3.4. Adsorption isotherm

Generally, the essential step in an inhibition mechanism is the adsorption of inhibitors on the steel surface [58]; therefore, the increase in corrosion inhibition is caused by the adsorption of inhibitors on the steel surface. To describe the adsorption of 2-butyne-1,4-diol on the steel surface, several adsorption isotherms were tested, including Freundlich, Temkin, Frumkin, Bockris–Swinkels, Flory–Huggins and Langmuir isotherms. However, the best agreement was obtained using the Langmuir adsorption isothermal equation as follows:

$$\frac{\theta}{1-\theta} = K_{ads} \cdot c \quad (6)$$

where $c$ is the concentration of the inhibitor, $K_{ads}$ is the adsorptive equilibrium constant and $\theta$ is the degree of surface coverage of the inhibitor molecule, which is given by the following equation:

$$\theta = \frac{R_{ct(0)} - R_{ct(inh)}}{R_{ct(0)}} \quad (7)$$

where $R_{ct(0)}$ and $R_{ct(inh)}$ are the charge transfer resistance in the absence and presence of inhibitors, respectively. Consequently, if the Langmuir isotherm describes the inhibitor adsorption process, a plot of experimental data expressed as ($c/\theta$) vs. ($c$) should yield a straight line with a linear correlation coefficient ($r$) and slope very close to unity. For both the EIS and weight loss experiments and the Langmuir isotherm data, the agreement was very good ($r^2 = 0.999$), which indicated an excellent inhibition of steel corrosion through the adsorption of 2-butyne-1,4-diol on the steel surface. The superiority of this process was also confirmed by the good agreement between the values obtained from the polarization and impedance studies and weight loss measurements.

However, the width of the original value of the ($c/\theta$) versus ($c$) plots showed little deviation from zero, which signified non-ideal and unexpected deviations from the Langmuir adsorption isotherm.

Table 4
EIS parameters obtained from the corrosion of steel 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution for different immersion times at 25 °C (the concentration of 2-butyne-1,4-diol was 5 mM).

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>$C_m$ ($\mu F \ cm^{-2}$)</th>
<th>$R_i$ ($\Omega \ cm^2$)</th>
<th>$R_0$ ($\Omega \ cm^2$)</th>
<th>CPE ($\mu F \ cm^{-2}$)</th>
<th>$n$</th>
<th>$K_a$ ($\Omega \ cm^2$)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5160</td>
<td>5.968</td>
<td>22.72</td>
<td>402</td>
<td>0.85</td>
<td>38.0</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>820</td>
<td>5.876</td>
<td>144.16</td>
<td>96</td>
<td>0.85</td>
<td>237.5</td>
<td>0.840</td>
</tr>
<tr>
<td>2</td>
<td>675</td>
<td>3.951</td>
<td>182.76</td>
<td>73</td>
<td>0.86</td>
<td>292.3</td>
<td>0.870</td>
</tr>
<tr>
<td>3</td>
<td>387</td>
<td>5.607</td>
<td>313.01</td>
<td>71</td>
<td>0.87</td>
<td>500.0</td>
<td>0.924</td>
</tr>
<tr>
<td>4</td>
<td>402</td>
<td>5.419</td>
<td>296.84</td>
<td>109</td>
<td>0.87</td>
<td>493.5</td>
<td>0.923</td>
</tr>
<tr>
<td>6</td>
<td>381</td>
<td>5.409</td>
<td>303.55</td>
<td>115</td>
<td>0.88</td>
<td>506.7</td>
<td>0.925</td>
</tr>
</tbody>
</table>
immersion time was 3 h). Generally, values of $D$ negative values of more than (physisorption) and the charged metal (physical adsorption), while with electrostatic interaction between the adsorbent and adsorbate $D$ ent study, the value of to form a coordinate type of bond (chemisorption)[31]. In the pres-
ter transfer of electrons from inhibitor molecules to the steel surface

cannot be ignored. In other words, in this case, acetylene alcohol

of oxygen atoms and the triple bond in acetylenic alcohol molecules

was mainly chemisorption. In fact, the role of non-paired electrons

bonding. Initial absorption likely takes place through the

triple bond, while hydroxyl groups reinforce the triple bond by giving
electrons to the steel surface. According to studies on the corro-
sion inhibition of 2-butyne-1,4-diol, the inhibition mechanisms
could include both physical absorption and absorption through the
sharing of electrons with the steel surface.

The $K_{ads}$ values showed the strength of the adsorption forces
between the inhibitor molecules and steel surface. According to
the values obtained for $K_{ads}$, the interaction between the double
layer that exists in the phase boundary and the adsorbed molecules
appeared to be relatively strong.

3.5. Surface morphology

The corrosion efficiency of 2-butyne-1,4-diol on steel in 2 M
$Na_2CO_3/1 M NaHCO_3$ was also clearly visible in Fig. 10, which
shows the steel surface topography in the testing electrolyte in
the absence and presence of the inhibitor. Fig. 10a shows the steel
surface in the solution before immersion. Fig. 10b demonstrates
that in the absence of the inhibitor, surface corrosion was exten-
sive and could clearly be seen in the form of significant surface
damage. The figure confirmed the presence of uneven corrosion
products arranged layer upon layer and in rough surface layers.
In contrast, in the presence of 5 mM 2-butyne-1,4-diol (Fig. 10c),
the steel surface was corroded only negligibly. In addition, there
was an adsorbed film on the steel surface that was not observed
in Fig. 10a. The result was an enhancement of surface coverage
on the steel surface such that there was a decrease in contact
between the steel and the aggressive medium. Thus, a good
absorptive protection layer can efficiently inhibit the corrosion of
steel.

3.6. AFM studies

The surface microstructure of the steel in 2 M $Na_2CO_3/1 M NaH-
CO_3$ solution before and after immersion and in the presence of
5 mM 2-butyne-1,4-diol after 3 h of immersion time was investi-
gated using AFM (Fig 11). The corroded surface in 2 M $Na_2CO_3/
1 M NaHCO_3$ solution in the absence of 2-butyne-1,4-diol looked
relatively uneven and appeared to have potholes, while it was rel-
atively flat and compact in the presence of 5 mM 2-butyne-1,4-diol
(Fig. 11(a)–(c)). It is clearly shown in Fig. 11(c) that the uncorroded

![Fig. 9. Langmuir isotherm adsorption model of 2-butyne-1,4-diol on the surface of steel in 2 M $Na_2CO_3/1 M NaHCO_3$ solution.](image)

![Fig. 10. (a) SEM image of steel surface taken after immersion in 2 M $Na_2CO_3/1 M NaHCO_3$ solution, (b) SEM image of steel surface taken after immersion in 2 M $Na_2CO_3/1 M NaHCO_3$ solution in the absence of 2-butyne-1,4-diol, (c) SEM image of steel surface taken after immersion in 2 M $Na_2CO_3/1 M NaHCO_3$ solution in the presence of 5 mM of 2-butyne-1,4-diol.](image)

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<th>$R_T$ ($\Omega cm^2$)</th>
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The corrosion of steel in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution was determined by SEM after immersion in 2 M Na$_2$CO$_3$/1 M NaHCO$_3$ solution at 25 °C and the results are shown in Fig. 11a, b and c. The corrosion of steel decreases after adding 5 mM 2-butyne-1,4-diol. The corrosion rate was lower than those in the absence of 2-butyne-1,4-diol. The inhibition efficiency increased, which confirmed adsorption of the inhibitor molecules on the steel surface, causing a decrease in surface roughness and effectively protecting the steel from corrosion. The equivalent circuit was selected based on properties of the EIS Nyquist diagrams and fit the experimental data well. The inhibition efficiencies were determined by polarization and EIS plots, which were in good agreement with the weight loss measurements. The changes in the impedance parameters confirmed the strong adsorption of the inhibitor on the steel surface, which prevented anodic dissolution of the metal by blocking active metal surface sites. Furthermore, in the presence of the inhibitor, the double layer capacitance decreased, which confirmed adsorption of the inhibitor molecules on the steel surface. The SEM results showed the formation of a protective and dense layer on the steel surface in the presence of the inhibitor.

References


A. Döner, R. Solmaz, M. Özcan, G. Kardas, Experimental and theoretical studies of thiazoles as corrosion inhibitors for mild steel in sulphuric acid solution, Corrosion Science 53 (2011) 2902–2913.


