Synergistic Inhibition Effect of 10-(3-Quinuclidinyl-Methyl) Phenothiazine and Potassium Iodide on Carbon Steel Corrosion in Sulfuric Solution

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Abstract: The inhibition effect of 10-(3-quinuclidinylmethyl) phenothiazine (QMPT), Potassium iodide and their synergistic effect on the corrosion of carbon steel in 0.5 M H₂SO₄ solution was studied by different electrochemical techniques. The inhibition efficiency increases with QMPT and KI concentration and increase further in presence of QMPT/KI mixtures. The adsorption of QMPT and KI on the metal surface in 0.5 M H₂SO₄ solution obeys the Langmuir adsorption isotherm. The probable inhibitory mechanism is proposed from the viewpoint of adsorption theory. The synergism parameter suggests that there is a cooperative mechanism between the iodide anion and QMPT cations.

Keywords: Corrosion inhibitor, Synergism, Iodide ion, Adsorption, EIS.

1. Introduction

Carbon steel is used in mass amounts in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment [1], despite it has a relatively high cost. These applications usually induce serious corrosive effects on equipment’s, tubes and pipelines made of iron and its alloys. The use of corrosion inhibitors is one of the most effective measures for protecting metal surfaces against corrosion in acidic environments [2]. Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys. A literature survey shows that most of the organic inhibitors will act upon adsorption onto the metal surface. The adsorption of inhibitors takes place through hetero-atoms such as nitrogen, oxygen, phosphorus, and sulfur, as well as through triple bounds or aromatic rings. The inhibition efficiency is reported to increase in the order O < N < S < P [3]. Synergistic inhibition is an effective means to improve the inhibiting force of the inhibitor, to decrease the amount of usage and to diversify the application of the inhibitor in acidic media. It is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. It is generally observed that the addition of halide ions to the corrosive media increases the adsorption ability of organic cations by forming interconnecting bridges between negatively charged metal surface and inhibitor cations. The order of synergism of halide ions is I⁻ > Br⁻ > Cl⁻. Since it has a larger size and ease polarizability, I⁻ ions are adsorbed on metal surface and provide better synergistic effect [4]. To our surprise, neither the inhibiting ability of 10-(3-quinuclidinylmethyl) phenothiazine (QMPT) (Figure 1) nor the synergistic effects with iodide ions toward the acid corrosion of carbon steel have been previously studied.

In the present a new corrosion inhibitor (QMPT), KI and their synergistic effect have been investing their inhibition effect on the corrosion of carbon steel in 0.5 M H₂SO₄ solutions by different electrochemical techniques.

2. Experimental

The inhibitor solutions of QMPT were prepared in 0.5 M H₂SO₄. The corrosion tests were performed in 0.5 M H₂SO₄ solution in the absence and presence of various concentrations of QMPT and/or KI. 0.5 M H₂SO₄ solution was prepared by dilution of 98% H₂SO₄ with distilled water. For each experiment, a freshly prepared solution was used under air atmosphere without stirring at 298 K.

Tests were performed on a carbon steel of the following 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. The electrochemical measurements were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. Carbon steel coupons having the area of 1 cm² were used as a working electrode. The working electrode was immersed in test solutions for 30 minutes to a establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp}, the electrochemical measurements were performed. The EIS experiments were conducted in the frequency range with
high limit of $10^5$ Hz and different low limit $10^{-2}$ Hz at open circuit potential. The polarization curves were obtained in the potential range from $-900$ to $-200$ mV (SCE) with 0.5 mV s$^{-1}$ scan rate.

3. Results and Discussion

3.1. Open Circuit Potential versus Time Measurements

Figure 2 shows the variation of the potential of carbon steel as a function of time in aerated 0.5 M H$_2$SO$_4$ solutions in the absence and presence of various concentrations of QMPT, KI and QMPT/KI mixture at 298 K.

![Figure 2: OCP at absence and presence of the investigated inhibitors](image)

In inhibitor-free sulfuric acid solution, the OCP changed quickly towards negative values, indicating the initial dissolution process of the pre-immersion air formed oxide film and the attack on the bare metal. In inhibited sulfuric acid solution the steady state $E_{corr}$ drifts to positive values in case of KI and QMPT/KI mixture. While in case of QMPT the steady state $E_{corr}$ drifts to more negative values. According to Riggs [5], the classification of a compound as an anodic or cathodic type inhibitor is feasible when the OCP displacement is at least 85 mV. Inspection of Table 1 reveals that the values of OCP displacement were about $-59.9$ to $-77.8$ mV in the presence of individual KI, and $-38.1$ mV in the presence of QMPT/KI mixture. While, the values of OCP displacement were about $103.1$ to $113.2$ mV in the presence of QMPT only.

![Table 1: OCP of the investigated inhibitors](image)

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$C$ (M)</th>
<th>$-E_{corr}$ (mV vs. SCE)</th>
<th>$E_{corr}$(inhibited) $- E_{corr}$(inhibited)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>543.7</td>
<td>-</td>
</tr>
<tr>
<td>QMPT</td>
<td>0.0001</td>
<td>646.8</td>
<td>103.1</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>649.8</td>
<td>106.1</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>656</td>
<td>112.3</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>656.9</td>
<td>113.2</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>438.8</td>
<td>-59.9</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>479.1</td>
<td>-64.6</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>475.3</td>
<td>-68.4</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>465.9</td>
<td>-77.8</td>
</tr>
<tr>
<td>QMPT + KI</td>
<td>0.005 + 0.005</td>
<td>505.6</td>
<td>-38.1</td>
</tr>
</tbody>
</table>

It is clear that the QMPT molecules are adsorbed on the anodic sites more than cathodic sites, resulting an inhibition of anodic than cathodic reactions, i.e. KI acts as mixed-type inhibitor with a predominant anodic inhibitor. In case of a mixture of KI and QMPT the mixture molecules are adsorbed on both anodic and cathodic sites, resulting in an inhibition of the both anodic and cathodic reactions, i.e. QMPT/KI mixture act as mixed-type inhibitor [6]. Therefore, the adsorption of QMPT/KI mixture on the carbon steel surface is more than individual QMPT or KI.

3.2. Tafel Polarization Measurements

The potentiodynamic polarization curves of carbon steel in 0.5 M H$_2$SO$_4$ solution in the absence and presence of various concentrations of QMPT, KI and QMPT/KI mixture are shown in Figures 3–5, respectively.

![Figure 3: Polarization plots of QMPT](image)

![Figure 4: Polarization plots of KI](image)

![Figure 5: Polarization plots of QMPT/KI mixture](image)

The values of related electrochemical parameters, i.e. corrosion current density ($i_{corr}$), $E_{corr}$ (vs. SCE), cathodic Tafel slope ($\beta_c$), anodic Tafel slope ($\beta_a$) and the inhibition efficiency ($\eta$) deduced from the polarization curves are...
summarized in Table 2. The inhibition efficiencies for different inhibitor concentrations were calculated from the following equation [7]:

$$\eta_i = \left( \frac{i_{corr} - i_{corr}^t}{i_{corr}} \right) \times 100$$  (1)

where \(i\) and \(i^t\) are uninhibited and inhibited corrosion current densities, respectively. As it can be clearly seen from Figure 3 that, the addition of QMPT to the corrosive solution both reduces anodic dissolution of iron and also retards cathodic hydrogen evolution reactions. The corrosion current density of steel considerably reduced in the presence of the QMPT and the inhibition \(\eta_i\) is more and more pronounced with the increasing QMPT concentration. These results are indicative of the adsorption of QMPT molecules on the carbon steel surface.

**Table 2:** Potentiodynamic electrochemical parameters of the investigated inhibitors at 298 K

| Inhibitors | \(C (M)\) | \(E_{corr} (mV_{ref})\) | \(i_{corr} (mA.cm^{-2})\) | \(\beta_a (mV_{dec}^{-1})\) | \(\beta_c (mV_{dec}^{-1})\) | \(\eta_i\) (%)
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>538.7</td>
<td>2.1876</td>
<td>224</td>
<td>208.2</td>
<td>–</td>
</tr>
<tr>
<td>QMPT</td>
<td>0.0001</td>
<td>647.4</td>
<td>1.7392</td>
<td>184.3</td>
<td>205.2</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>648.5</td>
<td>1.1477</td>
<td>150.8</td>
<td>153.9</td>
<td>47.5</td>
</tr>
<tr>
<td>KI</td>
<td>0.0001</td>
<td>648.9</td>
<td>0.738</td>
<td>133.2</td>
<td>174.8</td>
<td>66.3</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>479.9</td>
<td>1.0177</td>
<td>208.8</td>
<td>209.7</td>
<td>53.5</td>
</tr>
<tr>
<td>QMPT + KI</td>
<td>0.0001</td>
<td>487.4</td>
<td>0.3658</td>
<td>188.6</td>
<td>185.3</td>
<td>83.3</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>489.2</td>
<td>0.3586</td>
<td>219</td>
<td>188.7</td>
<td>83.6</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>486.3</td>
<td>0.3261</td>
<td>121.6</td>
<td>187.9</td>
<td>85.1</td>
</tr>
</tbody>
</table>

Inspection of Table 2 reveals that the corrosion potential was shifted to more negative potential values in comparison with corrosion potential observed in blank solution. These results suggest that QMPT can be classified as the cathodic type corrosion inhibitor. Figure 4 shows the polarization curves for carbon steel in 0.5 M H\(_2\)SO\(_4\) solution containing various concentrations of KI at 298 K. It is apparent that \(i_{corr}\) decreases considerably in the presence of iodide ions, and decreases with increasing the inhibitor concentration. Correspondingly, \(\eta_i\) increases with the inhibitor concentration, due to the increase in the blocked fraction of the electrode surface by adsorption. The presence of KI shifts \(E_{corr}\) to small negative value, which indicates that KI acts as a mixed-type inhibitor with predominant anodic inhibitor. It is observed that the combinations of 0.005 M KI and 0.005 M QMPT produce pronounced effects on the corrosion current density compared to those displayed by individual KI or QMPT (Figure 5). According to data of Table 2, the corrosion current density decreases substantially, leading to higher inhibition efficiency of QMPT/KI mixture, up to 96.3%, compared to 86.9 and 85.1% obtained for alone 0.005 M of QMPT and KI, respectively. This indicates a synergistic inhibition effect between QMPT and KI [8]. These results are in good agreement with those obtained from the OCP results.

3.3. Electrochemical Impedance Spectroscopy (EIS)

Figures 6–8 show the Nyquist plots for carbon steel in 0.5 M H\(_2\)SO\(_4\) solution in the absence and presence of QMPT, KI and QMPT/KI mixture at 298 K, respectively. The impedance diagrams consist of a large capacitive loop at high frequencies followed by a small inductive loop at low frequency values. The high frequency capacitive loop is usually related to the charge transfer of the corrosion process and double layer behavior. On the other hand, the low frequency inductive loop may be attributed to the relaxation process obtained from adsorption species like FeSO\(_4\) or inhibitor species on the electrode surface. It might be also attributed to the re-dissolution of the passivated surface at low frequencies. Furthermore, the diameter of the capacitive loop in the presence of inhibitors is bigger than that with the uninhibited solution and increases with the inhibitor concentrations. This indicates that the impedance of carbon steel corrosion increases with the inhibitor concentration and increases further in presence of a QMPT/KI mixture (Figure 8). The capacitive loops are not perfect semicircles which can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface [9].
where $\eta_i$ are found to increase with increasing the inhibitor concentration, while the values of $C_{dl}$ are found to decrease. This behavior was the result of an increase in the surface coverage by the inhibitor molecules, which led to an increase in the inhibition efficiency. The decrease in $C_{dl}$ values may be considered in terms of Helmholtz model [12]:

$$C_{dl} = \frac{e_0 \varepsilon A}{d}$$  \hspace{1cm} (5)

where $\varepsilon_0$ is the permittivity of air, $\varepsilon$ the local dielectric constant, $d$ the thickness of the film and $A$ is the surface area of the electrode. In fact, the decrease in $C_{dl}$ values can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer. It could be assumed that the decrease of $C_{dl}$ values is caused by the gradual replacement of water molecules by adsorption of inhibitor molecules on the electrode surface, which decreases the extent of the metal dissolution. The inhibition efficiencies calculated from EIS (Table 3), showed the same trend as those obtained from potentiodynamic polarization (Table 2). The curves are characterized by high frequency capacitance and small frequency inductive loops. As it is shown in Figure 8, the $R_{ct}$ values increase in the presence of QMPT/KI mixture than individual QMPT or KI, indicating the inhibition of the corrosion process while the double layer capacitance ($C_{dl}$) values decrease. The inhibiting effect of iodide ions is often attributed to its adsorption on the metal surface which depends on its large ionic radius and high hydrophobicity. The impedance spectra for the Nyquist plots were analyzed by fitting to the equivalent circuit model shown in Figure 9, which has been used previously to model the steel/acid interface [13].

$$Z_{CPE} = \frac{1}{j\omega C_{CPE}}$$  \hspace{1cm} (6)

The circuit comprises a solution resistance $R_s$ shorted by a constant phase element (CPE) that is placed in parallel to the charge transfer resistance $R_{ct}$. The value of the charge transfer resistance is indicative of electron transfer across the interface. The use of the CPE has been extensively described in the literature [14] and is employed in the model to compensate for the inhomogeneities in the electrode surface as depicted by the depressed nature of the Nyquist semicircle. The introduction of such a CPE is often used to interpret data for rough solid electrodes. The impedance, $Z$, of the CPE is:

$$Z_{CPE} = \left[\frac{Q(j\omega)^n}{j\omega}\right]^{-1}$$  \hspace{1cm} (6)

where the coefficient $Q$ is a combination of properties related to different physical phenomena like surface inhomogeneity, electro-active species, inhibitor adsorption, porous layer formation, etc., $j$ is an imaginary number ($j^2 = -1$), $\omega$ is the angular frequency ($\omega = 2\pi f$) and the exponent $n$ has values between $-1$ and $1$. A value of $-1$ is a characteristic for an inductance, a value 1 corresponds to a resistor, and a value of 0.5 can be assigned to the diffusion phenomenon.

### 3.4. Adsorption Isotherm

Several isotherms including Frumkin, Langmuir, Temkin, Freundlich, Bockris–Swinkels and Flory–Huggins isotherms are employed to fit the experimental data. It is found that the adsorption of studied QMPT and KI on the carbon steel surface obeys Langmuir adsorption isotherm equation:

$$Q = \frac{N A d}{V}$$  \hspace{1cm} (7)

where $N$ is the number of inhibitor molecules adsorbed on the electrode, $A$ is the area of the electrode, $d$ is the thickness of the adsorbed layer and $V$ is the volume of the solution. The values of $Q$ are calculated in Table 3. The electrochemical parameters derived from Nyquist plots are calculated and listed in Table 3. The values of charge transfer resistance ($R_{ct}$) were given by subtracting the high frequency impedance from the low frequency one as follows [10]:

$$R_{ct} = Z \| (at \ low \ frequency) - Z \| (at \ high \ frequency)$$  \hspace{1cm} (2)

The values of percentage inhibition efficiency ($\eta_i$) were calculated from the values of $R_{ct}$ according to the following equation [11]:

$$\eta_i = \left(\frac{R^0_{ct} - R_{ct}}{R^0_{ct}}\right) \times 100$$  \hspace{1cm} (4)

where, $R^0_{ct}$ and $R_{ct}$ are the values of the charge transfer resistance in the presence and absence of inhibitor, respectively.

### Table 3: Impedance electrochemical parameters

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>$C$ (M)</th>
<th>$R_d$ (ohm.cm$^2$)</th>
<th>$C_{dl}$ (µF.cm$^{-2}$)</th>
<th>$\eta_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>23</td>
<td>246.7</td>
<td>-</td>
</tr>
<tr>
<td>QMPT</td>
<td>0.0005</td>
<td>32.2</td>
<td>170.9</td>
<td>30.7</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>48.5</td>
<td>116.9</td>
<td>52.6</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>93.3</td>
<td>60.7</td>
<td>75.4</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>213.7</td>
<td>26.6</td>
<td>89.2</td>
</tr>
<tr>
<td>KI</td>
<td>0.0001</td>
<td>49.7</td>
<td>114.2</td>
<td>53.7</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>157.3</td>
<td>36</td>
<td>85.4</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>168.1</td>
<td>33.8</td>
<td>86.3</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>181.6</td>
<td>31.3</td>
<td>87.3</td>
</tr>
<tr>
<td>QMPT + KI</td>
<td>0.0005</td>
<td>435.1</td>
<td>13.1</td>
<td>94.7</td>
</tr>
</tbody>
</table>

The impedance data listed in Table 3 indicate that the values of both $R_d$ and $\eta_i$ are found to increase with increasing the inhibitor concentration, while the values of $C_{dl}$ are found to decrease. This behavior was the result of an increase in the surface coverage by the inhibitor molecules, which led to an increase in the inhibition efficiency. The decrease in $C_{dl}$ values may be considered in terms of Helmholtz model [12]:

Figure 8: Nyquist plots of QMPT/KI mixture

Figure 9: The equivalent circuit model
where, \( C \) is the concentration of inhibitor, \( K_{ads} \) the adsorptive equilibrium constant and \( \theta \) is the degree surface coverage (\( \theta = \eta / 100 \)). The degree of surface coverage values for various concentrations of QMPT and KI in the 0.5 M H\(_2\)SO\(_4\) solution have been calculated from the average of inhibition efficiency of potentiodynamic polarization and electrochemical impedance measurements (Table 2&3). Plots of \( C/\theta \) against \( C \) yield straight lines as shown in Figure 10. Both linear correlation coefficient (\( r \)) and slope are close to 1, indicating the adsorption of the investigated inhibitors on the carbon steel surface obeys Langmuir adsorption isotherm. The adsorptive equilibrium constant (\( K_{ads} \)) can be calculated from the reciprocal of the intercept of \( C/\theta-C \) curve. The values of \( K_{ads} \) were calculated as 2747.3 M\(^{-1}\) for QMPT and 25641 M\(^{-1}\) for KI. The high value of \( K_{ads} \) attribute to the stronger and more stable adsorbed layer formed on the metal surface. The standard free energy of adsorption (\( \Delta G_{ads}^o \)) can be given as the follows:

\[
\Delta G_{ads}^o = -RT \ln(55.5K_{ads})
\]

(8)

where, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) the absolute temperature (K), and the value 55.5 is the concentration of water in solution expressed in molar. The high values of \( K_{ads} \) and negative values of \( \Delta G_{ads}^o \) suggested that, inhibitor molecules strongly adsorbed on the carbon steel surface. Values of \( \Delta G_{ads}^o \) around \(-20 \) kJ mol\(^{-1}\) or lower are consistent with the electrostatic interaction between charges inhibitor molecules and the charged metal surface (physisorption); those around \(-40 \) kJ mol\(^{-1}\) or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption). The obtained values of \( \Delta G_{ads}^o \), were \(-30 \) and \(-36 \) kJ mol\(^{-1}\) for QMPT and KI, respectively. This indicates that the adsorption takes place mainly through the electrostatic interaction between charges inhibitor molecules and the charged metal surface (physisorption) [14].

It was found that the inhibition efficiency of solutions of QMPT/KI mixture exhibit higher values compared to solutions of individual QMPT or KI. This reflects that KI has a synergistic inhibiting effect on the carbon steel corrosion in 0.5 M H\(_2\)SO\(_4\) solution. This can be explained by the strong adsorption of iodide ions on the metal surface. The QMPT molecules are then adsorbed by colubmic attraction on the metal surface. Stabilization of the adsorbed iodide ions with the inhibitor leads to greater surface coverage and thereby greater inhibition. The iodide ions enhance the stability of the inhibitor on the metal surface by a co-adsorption mechanism, which may be either be competitive or cooperative [16]. For competitive adsorption, the anions and the inhibitor cations are adsorbed at different sites on the metal surface. In cooperative adsorption, the anions are adsorbed on the metal surface and the cations are adsorbed on a layer of the anions. Competitive and cooperative mechanisms may occur simultaneously in some cases. Generally, values of \( S < 1 \) imply that antagonistic behavior prevails, which may lead to competitive adsorption, whereas \( S > 1 \) indicates a synergistic effect [17]. Inspection of Table 4 shows that values of \( S \) were greater than unity. This may suggest that the enhanced inhibition efficiency caused by the addition of iodide ions to the QMPT molecules was only due to synergistic effect.

### 3.6. Inhibition mechanism

The corrosion mechanism of carbon steel in H\(_2\)SO\(_4\) medium is under anodic control which is [18]:

\[
\text{Fe} + \text{H}_2\text{O} \leftrightarrow [\text{FeOH}]_{ads} + \text{H}^+ + \text{e}^{-} \quad (10)
\]

\[
[\text{FeOH}]_{ads} \rightarrow [\text{FeOH}]^+ + \text{e}^{-} \quad (11)
\]

\[
[\text{FeOH}]^+ + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O} \quad (12)
\]

The mechanism of corrosion inhibition of carbon steel in 0.5 M H\(_2\)SO\(_4\) by QMPT may be deduced on the basis of adsorption. In acidic solutions, this inhibitor can exist as
cationic species (Eq. (11)) which may be adsorbed on the cathodic sites of the carbon steel (as discussed in the Tafel polarization section) and reduce the evolution of hydrogen:

\[ \text{QMPT} + x \text{H}^+ \leftrightarrow [\text{QMPTH}\d^{x^+}] \quad (13) \]

The charge on the metal surface can be determined from the value of \( E_{OCP} - E_{q=0} \) (zero charge potential (vs. SCE)) [19]. As reported from a survey, the \( E_{q=0} \) of iron is \(-550\) mV versus SCE in H\(_2\)SO\(_4\) [20]. In the present system, the value of \( E_{OCP} \) obtained in 0.5 M H\(_2\)SO\(_4\) is \(-543.7\) mV versus SCE. So the charges of steel surface are positive charge in H\(_2\)SO\(_4\) because of \( E_{OCP} - E_{q=0} > 0 \). Since the acid anions of SO\(_4^{2-}\) could be specifically adsorbed, they create an excess negative charge towards the solution and favor more adsorption of the cations. In the presence of iodide ions, the mechanism of the anodic dissolution is given as:

\[ \text{Fe} + \text{H}_2\text{O} + \Gamma \leftrightarrow [\text{FeOH}]_{\text{ads}} + \text{H}^+ + e^- \quad (14) \]

\[ [\text{FeOH}]_{\text{ads}} \rightarrow [\text{FeOH}] + e^- \quad (15) \]

\[ [\text{FeOH}] + \text{H}^+ \rightarrow \text{Fe}^{2+} + \Gamma + \text{H}_2\text{O} \quad (16) \]

The QMPT molecules may then combine with the adsorbed intermediates to form metal-inhibitor complex. The resulting complexes could either catalyze or inhibit further metal dissolution depending on its solubility [21]. From the results obtained in this study, the \( \Gamma^- \) ions form insoluble complexes with QMPT molecules leading to reduction in corrosion rate and raised inhibition efficiency. The highest synergistic effect of iodide ions has been attributed to adsorption with metal surface due to its larger size, ease of polarizability, high hydrophobicity and low electronegativity compared to the other halide ions [22]. The strong adsorption of iodide ions on the metal surface is responsible for the synergistic effect of iodide ions in combination with QMPT molecules. Then the QMPT molecules are adsorbed by coulombic attraction at the metal surface, where iodide ions are already adsorbed. Stabilization of the adsorbed iodide ions by means of electrostatic interaction with QMPT molecules leads to greater surface coverage and thereby greater inhibition efficiency. Another explanation of improved inhibition efficiency of iodide ions is the presence of iodide ions causing a positive shift in potential (vs. SCE) of zero charge (\( E_{OCP} - E_{q=0} > 0 \)) and makes the overall charge on the metal surface more negative (Table 1), which facilitates the adsorption of positively charged species [23].

4. Conclusions

QMPT and KI inhibit the corrosion of carbon steel in 0.5 M H\(_2\)SO\(_4\) solution and the inhibition efficiency increases with an increase inhibitor concentration and increase further in presence of QMPT/KI mixture. Tafel polarization studies showed that the QMPT acts as a cathodic inhibitor while KI act as mixed-type inhibitor with a predominant anodic inhibitor. The adsorption of QMPT and KI on the metal surface in 0.5 M H\(_2\)SO\(_4\) solution obeys the Langmuir adsorption isotherm. There is a synergism between QMPT and KI, and the values of synergism parameter (\( S \)) are higher than unity. The synergism parameter suggests that there is a cooperative mechanism between the iodide anion and QMPT cations.

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References


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