Study on the Synergistic Inhibition Effect of Imidazoline and Mercaptoethanol on the Corrosion of Carbon Steel in Tarim Oilfield

Cheng-xin YANG\textsuperscript{1*}, Yu-shuang LIU\textsuperscript{2}, Yong LIU\textsuperscript{1}, Long LI\textsuperscript{2}, Ping-liang FANG\textsuperscript{2}, Zhao HUANG\textsuperscript{2}, Mu LI\textsuperscript{2} and Yu-ping YANG\textsuperscript{2}

\textsuperscript{1}Petrochina Tarim Oilfield Company, Kuerle 841000, China
\textsuperscript{2}CNPC Engineering Technology R&D Company Limited, Beijing 102206, China

\*Corresponding author

Keywords: Carbon steel, Carbon dioxide corrosion, Inhibitor, Synergistic inhibition effect, Imidazoline, Mercaptoethanol.

Abstract. The inhibition effect of oleic-based imidazoline (OIM) and mercaptoethanol (ME) on the corrosion of carbon steel in carbon dioxide saturated 3.5\% sodium chloride solution was investigated by weight-loss method, electrochemical techniques and scanning electron microscopy (SEM) analysis. Results indicate that compared with individual addition of OIM or ME, better corrosion inhibition effect can be obtained when OIM-ME mixture is added. The OIM-ME mixture can inhibit both anodic and cathodic reactions, significantly alleviating the corrosion of carbon steel. Morphologies analysis also confirms the excellent inhibition effect of OIM-ME mixture. Thus, a conclusion can be drawn that there is notable synergistic inhibition effect between OIM and ME, and the optimal molar ratio of OIM and ME is 1:3.

Introduction

Carbon dioxide is usually found in oil and gas exploitation in Tarim oilfield. And carbon dioxide could be very corrosive to metallic equipment when it is dissolved into produced liquid [1-2]. The dissolution of carbon dioxide into produced liquid can lead to the decrease of pH value, resulting in severe acidic corrosion. This kind of corrosion is usually known as “sweet corrosion”, which is a major problem in the oil and gas industry [3].

Carbon steels are widely used in oilfield system, due to their relatively low cost, good machining performance and acceptable corrosion resistance. However, carbon steel equipment is quite sensitive to “sweet corrosion” environment and easily corrode. Among numerous corrosion protection methods, corrosion inhibitor is widely used and acts as one of the most economical and effective ways to defend corrosion attack in industrial areas [4-5]. Imidazoline and its derivatives have been used extensively as corrosion inhibitors in present petroleum industry for their outstanding anticorrosion performance [6-8]. In order to obtain better corrosion inhibition performance and reduce the applied dosage, mixtures of various chemicals with imidazoline are commonly used together in practice to produce a synergistic effect.

In this paper, the synergistic effect of OIM and ME on the corrosion of carbon steel in carbon dioxide saturated 3.5\% sodium chloride solution at 65 °C was studied by weight-loss method and electrochemical measurement. In addition, the surface morphology observation by using SEM has also been performed to confirm the synergistic effect.

Experiment

Experimental Samples

Chemical composition of carbon steel (Q235) used in this study is listed in Table 1. All samples were ground to P2000 grit SiC paper, rinsed in an ultrasonic bath with acetone, and dried in cold air before experiments.
Experimental Solution

3.5% sodium chloride solution was used as the blank solution. The pH value of the solution, saturated with carbon dioxide gas, was 4.3 (65 °C).

The purity of OIM (Shengli Co. Ltd., China) is approximately 96%. ME (Kelong Co. Ltd., China) was analytical grade. The inhibitor concentration of OIM and ME was 2×10⁻⁴ mol•L⁻¹. The experiment temperature was 65 °C.

Weight-loss Measurements

Samples with the size of 40 mm×13 mm×2 mm were immersed in flasks with a total volume of 500 ml 3.5% sodium chloride solution. Prior to the test, carbon dioxide was introduced into the solution for 1 hour (h) to remove oxygen. After immersion for 72 h, samples were taken out of the corrosive electrolyte and the surface corrosion products were removed by chemical descaling solution (10% hydrochloric acid + 0.5% Ammonioformaldehyde) in ultrasonic cleaner for 5 min. All samples were weighed by an analytical balance (with a precision of 0.1 mg) before and after the tests. Tests were conducted three times for each condition.

SEM Morphology Analysis

Corrosion morphology analysis was also carried out through SEM instrument (ZEISS EOV 18, Germany). Samples were immersed in CO₂-saturated 3.5% NaCl solution in the absence and presence of individual OIM, ME or OIM-ME for 12 h, then rinsed with deionized water and dried for morphology observation.

Electrochemical Experiments

The electrochemical measurements were carried out by a potentiostat (Holland IviumStat). A conventional three electrodes cell composed of working electrode (WE), saturated calomel reference electrode (SCE) with a Luggin capillary salt bridge and a platinum counter electrode (CE) was used. The WE surface area exposed to the aggressive solution was 1 cm². The test temperature was 65±1 °C. Saturated carbon dioxide condition was obtained by passing carbon dioxide gas into 3.5% sodium chloride solution for 1 h before tests and all through the electrochemical experiments.

The potentiodynamic polarization measurements were conducted after 2 h in-situ monitoring of OCP in both inhibited and uninhibited solution. The potential was scanned from -500 to +700 mV (vs. OCP), with scan rate of 0.5 mV•s⁻¹.

Results and Discussion

Weight-loss Measurement

Corrosion rates (CRs) of carbon steel and the inhibition efficiencies (IE%) of corrosion inhibitors from weight-loss measurement are listed in Table 2.

The corrosion rates (CRs) of the carbon steel were calculated by using Eq. 1:

CR = Δm / St.                                                                                               (1)

where Δm is the average weight loss of three identical samples, S is the exposed surface area of the sample and t is immersion time.

And the inhibition efficiencies (IE%) of the corrosion inhibitors were calculated by the corrosion rates (CRs) using Eq. 2:

Table 1. Chemical composition of carbon steel used in this study (wt.%).

<table>
<thead>
<tr>
<th>Component</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>0.16</td>
<td>0.30</td>
<td>0.53</td>
<td>0.015</td>
<td>0.004</td>
<td>bal</td>
</tr>
</tbody>
</table>

The potentiodynamic polarization measurements were conducted after 2 h in-situ monitoring of OCP in both inhibited and uninhibited solution. The potential was scanned from -500 to +700 mV (vs. OCP), with scan rate of 0.5 mV•s⁻¹.
IE% = (1 - CR/ CR′) \times 100\%.

where CR and CR′ are the corrosion rates of carbon steel in inhibited and uninhibited solution, respectively.

It is observed in Table 2 that the corrosion rate of carbon steel is very high in the blank solution. Carbon steel was seriously corroded. The addition of OIM or ME apparently alleviated the severity, indicating a protecting effect against carbon dioxide corrosion. An inhibition efficiency (IE%) of 73.1% and 56.3% for OIM and ME, respectively was obtained. Furthermore, the IE% values exceed 80% when OIM-ME mixtures are added, which reveals the apparent synergistic inhibition effect of OIM and ME. In addition, the maximum corrosion inhibition efficiency can reach 89.6% when the mole ratio of OIM:ME equals to 1:3.

Table 2. CRs and IE% values of carbon steel in the absence and presence of corrosion inhibitors (2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}) in carbon dioxide saturated solution at 65^\circ \text{C} by weight-loss measurements.

<table>
<thead>
<tr>
<th>Inhibitor addition</th>
<th>CR/(g \cdot m^{-2} \cdot h^{-1})</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>OIM</td>
<td>0.16</td>
<td>73.1</td>
</tr>
<tr>
<td>ME</td>
<td>0.25</td>
<td>56.3</td>
</tr>
<tr>
<td>OIM:ME=5:1</td>
<td>0.10</td>
<td>83.4</td>
</tr>
<tr>
<td>OIM:ME=3:1</td>
<td>0.09</td>
<td>85.6</td>
</tr>
<tr>
<td>OIM:ME=1:1</td>
<td>0.08</td>
<td>86.8</td>
</tr>
<tr>
<td>OIM:ME=1:3</td>
<td>0.06</td>
<td>89.6</td>
</tr>
<tr>
<td>OIM:ME=1:5</td>
<td>0.10</td>
<td>82.7</td>
</tr>
</tbody>
</table>

**Morphology Observation**

The surface morphologies of carbon steels in uninhibited and inhibited solution are shown in Figure 1. SEM images in Figure 1b showed that carbon steels in uninhibited solution severely corroded. Pits were randomly distributed and large amount of corrosion products were also observed, compared with original samples shown in Figure 1a. As presented in Figure 1c and Figure 1d, the addition of OIM or ME effectively alleviated the corrosion. Corrosion products were minimized, indicating a good corrosion inhibition performance. It is observed in Figure 1e that in presence of OIM-ME mixture (1:3), fresh scratches were visible and there were no signs of corrosion products, which suggested corrosion reactions were greatly suppressed. The application of OIM-ME combination exhibited much stronger inhibition performance than individual addition of OIM and ME, respectively, confirming the conclusion of synergistic inhibition effect drawn from weight-loss measurement.

**Potentiodynamic Polarization Experiment**

The OCP variations with time were presented in Figure 2a. It can be seen that the OCP value keeps at about -0.73 V in the absence of corrosion inhibitor. In the presence of inhibitor, the corrosion potential is higher in comparison, which indicates that the presence of corrosion inhibitor makes the metal surface more stable thermodynamically. It is also noticed that OCP values fluctuate significantly in the presence of inhibitor, especially in the presence of OIM. The fluctuations reveal the dynamic adsorption and equilibrium of corrosion inhibitors at the electrode/solution interface.

PC measurements also confirm the result, as shown in Figure 2b. With the addition of corrosion inhibitor, the corrosion potential (E_{corr}) becomes much nobler. Both the anodic and cathodic current densities decrease, which suggests the anodic dissolution process and the cathodic hydrogen evolution process have been retarded. And the changes of both anodic Tafel slope and cathodic Tafel slope are due to the adsorption of corrosion inhibitors. Furthermore, the addition of OIM-ME mixture can produce a stronger inhibition effect on both anodic dissolution and cathodic hydrogen evolution.
process than individual addition of OIM or ME. An abrupt increase of corrosion current can be
detected on the anodic curve in the presence of OIM-ME mixture when the polarization potential
reaches a relatively higher value (around -0.5 V). This involves an anodic desorption process of
corrosion inhibitors or the attack of Cl\textsuperscript{-1} on the protective film formed by inhibitors. Higher corrosion
potential could accelerate the desorption rate of corrosion inhibitors, strongly affecting the
adsorption-desorption equilibrium process. More desorption of adsorbed inhibitors leads to exposure
of metal substrate, promoting the corrosion of carbon steel and increasing corrosion current density.

By Tafel extrapolation method, anodic and cathodic Tafel slopes ($\beta_a$, $\beta_c$), corrosion potential ($E_{corr}$)
and corrosion current densities ($I_{corr}$) are calculated, as listed in Table 3. The values of inhibition
efficiency IE% are calculated by corrosion current densities ($I_{corr}$) from Eq. 3:

$$IE\% = \frac{(I'_{corr} - I_{corr})}{I'_{corr}} \times 100.$$  \hspace{1cm} (3)

where $I'_{corr}$ and $I_{corr}$ are the corrosion current densities without and with the addition of corrosion
inhibitors, respectively. Inhibition efficiencies (IE%) calculated from $I_{corr}$ are also listed in Table 3.

It is observed from Table 3 that in the presence of corrosion inhibitors, $E_{corr}$ remarkably increases.
And higher values of $E_{corr}$ are obtained when OIM-ME mixture is added. Besides, both the values of
anodic Tafel slope and cathodic slope have changed greatly in the presence of OIM-ME mixture,
confirming a mixed type of corrosion inhibitor. In addition, the corrosion current density ($I_{corr}$) sharply
decreases with addition of corrosion inhibitors, which indicates that the corrosion of carbon steel is
retarded. Compared with 78.5% and 61.7% inhibition efficiency for individual addition of OIM and
ME respectively, higher inhibition efficiencies for OIM-ME mixtures, 98.8% for OIM:ME=1:3, are
obtained, indicating an obvious synergistic inhibition effect between OIM and ME. These results are in good agreement with the weight-loss experiment, although there is some deviation of the IE%, due to different methods.

Table 3. Electrochemical parameters and inhibition efficiency obtained from polarization curves of carbon steel in the carbon dioxide saturated solution in the absence and presence of inhibitors at 65℃.

<table>
<thead>
<tr>
<th>Formula</th>
<th>βa/(mV)</th>
<th>βc/(mV)</th>
<th>Ecorr/(mV)</th>
<th>Icorr/(µA·cm⁻²)</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>242</td>
<td>205</td>
<td>-721</td>
<td>92.3</td>
<td>-</td>
</tr>
<tr>
<td>OIM</td>
<td>211</td>
<td>291</td>
<td>-582</td>
<td>19.8</td>
<td>78.5</td>
</tr>
<tr>
<td>ME</td>
<td>253</td>
<td>238</td>
<td>-635</td>
<td>35.5</td>
<td>61.7</td>
</tr>
<tr>
<td>5:1</td>
<td>205</td>
<td>208</td>
<td>-606</td>
<td>2.8</td>
<td>96.9</td>
</tr>
<tr>
<td>3:1</td>
<td>231</td>
<td>209</td>
<td>-623</td>
<td>2.3</td>
<td>97.5</td>
</tr>
<tr>
<td>1:1</td>
<td>221</td>
<td>206</td>
<td>-618</td>
<td>1.9</td>
<td>97.9</td>
</tr>
<tr>
<td>1:3</td>
<td>227</td>
<td>211</td>
<td>-601</td>
<td>1.1</td>
<td>98.8</td>
</tr>
<tr>
<td>1:5</td>
<td>179</td>
<td>224</td>
<td>-616</td>
<td>2.9</td>
<td>96.8</td>
</tr>
</tbody>
</table>

It is noticed both in the case of weight-loss experiment and potentiodynamic polarization measurement that the best corrosion inhibition effect can be observed, when OIM:ME=1:3. This reveals that at the ratio of 1:3, OIM-ME mixture can exhibit the optimal synergistic inhibition effect. The corrosion inhibition effect may be related to the geometric distribution of OIM and ME molecules at the solution/metal interface. The maximum synergistic inhibition effect appears when the most proper inhibitive film barrier of OIM and ME is formed. And further study on the synergistic mechanism will be investigated.

Conclusions

The synergistic inhibition effect of OIM and ME was investigated by weight-loss method, electrochemical measurements together with SEM analysis. The conclusions are summarized as follows:

1. The synergistic inhibition effect was found between OIM and ME on the corrosion of carbon steel in 3.5% sodium chloride solution saturated with carbon dioxide at 65 ℃.
2. The mixture exhibits the best synergistic corrosion inhibition effect when the molar ratio of OIM: ME equals to 1:3.
3. OIM-ME mixture is a mixed-type corrosion inhibitor. And its corrosion inhibition efficiency can reach up to 90% with 2×10⁻⁴ mol·L⁻¹ addition.

References


