Corrosion Inhibition of Steel C1018 with Novel Complexes of Imidazoline

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Abstract

New complexes of imidazolines with alkyl halogens were synthesized based on naphthenic acid and their inhibitive action against the corrosion of steel in CO2-saturated 1% NaCl solution were investigated at 50 °C. The results show that investigated complexes of imidazolines are good inhibitors and inhibition efficiency reaches 99% at 100 ppm. The high inhibition efficiencies were attributed to the simple blocking effect by adsorption of inhibitor molecules on the steel surface. The synthesized complexes were confirmed by physical-chemical methods and FT-IR spectra.

Keywords: Imidazolines Complexes, Corrosion, Inhibitors, Mild Steel, CO2 -Saturated Solution

1. Introduction

Corrosion of steel is a significant problem in the oil and gas production and transportation systems and causes significant economic loss (Miksic et al, 2004 and Song et al, 2004). Rupture as a result of corrosion of the pipe wall frequently causes failure of petroleum and gas pipelines. The breakdowns are followed by large losses of the products, environmental pollution and ecological disasters (Mikhailovskii et al, 1997). The majority of oil and gas pipelines failures result from CO2 corrosion of carbon and low alloy steels (Durnie et al, 2001 and Lopez et al, 2003) and occur at all stages of production from down hole to surface equipment and processing facilities (Fu et al, 1993). The mechanism of carbon dioxide corrosion is a complicated process that is influenced by many factors and conditions (Videm & Dugstad, 1989a and Kermani & Morshed, 1993). These range from pipeline and composition of the solution to other environmental factors (Videm & Dugstad, 1989b; Heuer & Stubbins, 1999; Olsson & Landolt, 2003 and Okafor & Nesic, 2007), however, significant progress has been achieved in understanding the mechanism of CO2 corrosion in the oil and gas industry (Nesic et al, 1996; De Waard & Milliams, 1997; Linter & Burststein, 1999; Nesic et al, 2003 and Nordsveen et al, 2003). The use of chemical inhibitors has been acknowledged as one, and a very practical and most economical, method of combating CO2 corrosion (Abd El-Lateef et al, 2012a and Abd El-Lateef et al, 2012b). The inhibiting molecule retards the rate of corrosion by acting at the metal–corrosive medium interface.

In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defence against corrosion. Most of the inhibitors currently used in producing wells are organic nitrogenous compounds. Once amines and imidazolines came into use, corrosion inhibition in oil wells became dramatically more effective. Nowadays, however, the inhibition mechanism of imidazoline remains poorly understood (Rodrıguez-Valdez et al, 2006).

In this work, the inhibition behaviour of the synthesized complexes of imidazolines with alkyl halogens in CO2-saturated 1% NaCl solution was investigated using linear polarization resistance corrosion rate technique. The results showed that, the synthesized complexes of imidazolines are good inhibitors for steel in CO2-saturated brine.
2. Experimental

The chemical composition of mild steel used in this study was given in (Abd El-Lateef et al, 2012a). The complex imidazolines as multifunctional reagents were synthesized in the laboratory on the basis of different fractions of naphthenic acids, Diethylenetriamin (DETA), Tri Ethylene Tetraamine (TETA) and Poly Ethylene Poliamine (PEPA). The product is alkyl imidazoline amines and their complexes containing two alkyl groups by connecting alkyl radicals to free amine groups. The synthesized imidazoline complexes can be illustrated by reaction Scheme 1. First imidazoline was obtained from interaction between naphthenic acid and PEPA. The reaction was carried out at temperature range of 130-140 °C.

\[
\text{RCOOH} + \text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{130-140 \degree C} \text{RCONH}(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2
\]

\[
\xrightarrow{240 \degree C} \text{RC} + \text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2 + \text{R'}\text{X} + \text{H}_2\text{O}
\]

\[
\left[ \text{RC} + \text{H}_2\text{O} \right] \xrightarrow{240 \degree C} \text{RCONH}(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2 + \text{R'}\text{X}
\]

Scheme 1. Reactions Scheme of the Synthesis of Imidazoline Complexes

Imidazoline was taken at different molar ratio (Table 1) with alkyl halogens at temperature range of 40-50 °C and for a period of 3 hours. The chemical structure of the synthesized complexes Imidazoline was characterized by physical-chemical spectroscopic methods (Table 2). Infrared spectra for the synthesized complexes were measured using a model FT-IR, Spectrum BX spectrometer using KBr disks.

The aggressive solution, 1% NaCl, was prepared by dissolving of analytical grade NaCl in distilled water. The concentration of the prepared imidazoline complexes was 100 ppm used for corrosion measurements. All solutions were prepared using isopropyl alcohol.

To study the corrosion, protection ability of the synthesized imidazoline complexes was used by one of the latest devices in recent years i.e. ACM GILL AC (manufactured by ACM Instruments). The apparatus consists of a monitor, CPU, potentiometer ACM GILL AC, four pieces of glasses with a capacity of 4000 ml, electrodes, CO₂ tank and installation- regulating the quantity fed CO₂. The prepared 1% - of the solution sodium chloride was stirred by a magnetic stirrer for 30 min in 4000 ml. The prepared solution was poured into the 4 glass beakers (1000 ml for each one). Beakers were then placed on a heater at 50 °C for 1 hour under 0.9 bars pressure. The solution was saturated with carbon dioxide. The electrodes were placed in the medium and were connected through a potentiometer ACM GILL AC. The surface of working electrode was cleaned by acetone before using (these electrodes are disposable in nature). After 1 hour, except for 1 beaker, the remaining 3 were fed with the suitable amount of inhibitor and continued the supply of CO₂ at a pressure of 0.9 bar till the end of the experiment.

The potential of the working electrode was varied by a Core Running program (Version 5.1.3.) through a
potentiometer ACM Gill AC. Gill AC technology allows measuring DC and AC signals using standard Sequencer software. A small sweep from typically -10mV to +10mV, at 10 mV/min around the rest potential is performed.

<table>
<thead>
<tr>
<th>Complex Name</th>
<th>Initiative Matter</th>
<th>Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-1</td>
<td>imidazole:C₅H₅Br</td>
<td>1:1</td>
</tr>
<tr>
<td>N-2</td>
<td>imidazole:C₅H₅Br</td>
<td>1:2</td>
</tr>
<tr>
<td>N-3</td>
<td>imidazole:C₅H₅Br</td>
<td>1:3</td>
</tr>
<tr>
<td>N-4</td>
<td>imidazole:C₅H₅Br</td>
<td>1:1</td>
</tr>
</tbody>
</table>

The Core Running program converts a corrosion current in mA/cm² to different relationships i.e. building on the density of electricity mA/cm², the corrosion rate of the time (mm/year or hour), loss of metal from time to time (mg/h).

Table 2. Physical-Chemical Properties of Imidazoline Complexes with Alkyl Halogens

<table>
<thead>
<tr>
<th>Complexes Name</th>
<th>Density, (d'_i) (g/cm³)</th>
<th>Refraction Coefficient ((\eta_o'))</th>
<th>Freezing Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-1</td>
<td>0.9290</td>
<td>1.4350</td>
<td>Minus 97</td>
</tr>
<tr>
<td>N-2</td>
<td>0.9739</td>
<td>1.4400</td>
<td>Minus 48</td>
</tr>
<tr>
<td>N-3</td>
<td>1.0316</td>
<td>1.4530</td>
<td>Minus 8 (not frozen)</td>
</tr>
<tr>
<td>N-4</td>
<td>0.9372</td>
<td>1.4400</td>
<td>Minus 12</td>
</tr>
</tbody>
</table>

Each experiment was performed with freshly prepared solution and clean set of electrodes. Measurements were conducted at temperature 50 °C for the investigated NaCl solution. For this purpose, Magnetic Stirrer with Heater (115 V, 50/60 Hz) was used.

3. Results and Discussion

3.1. Chemical Structure of the Synthesized Imidazolines Complexes

The structural characteristics of purified product were confirmed by FT-IR spectroscopy in the range 4000–500 cm⁻¹, as shown in Figure 1. IR spectrum of sample N-4 contains a series of absorption bands of varying intensity in the region 500–4000 cm⁻¹. In addition, there was a band at 733.03 cm⁻¹ indicating the presence of the pendular oscillations of C–H bond in C₅H₅ group. The band bending at 1468 cm⁻¹ and stretching vibrations at 2859.70, 2928.26 cm⁻¹, characteristic for the C–H bond of the methylene (CH₂) groups. The absorption bands of strong intensity of deformation at 1376.36 cm⁻¹ and stretching vibrations at 2954.90 cm⁻¹ corresponding to the C–H bond of the methyl (CH₃) groups. Stretching vibrations at 1647.71 cm⁻¹ indicating C=N bond. Stretching vibrations at 3420.38 cm⁻¹ was due to R-NH₂ bond. Deformation vibrations at 1606.34 cm⁻¹ was due to N-H bond in the NH₂ group, but at 1541.02 cm⁻¹ for N-H bond of the NH group. Stretching band at 1122.36 cm⁻¹ was due to C-NR₂ group, and at 1302.99 cm⁻¹ for R-NH-R group, but the stretching band at 3280 cm⁻¹ was for R-NH-R group. The results were generally in agreement with the expected correlations.

3.2. Effect of Imidazoline Complexes on the Corrosion Behaviour of Mild Steel in CO₂-Saturated Brine

The inhibitive corrosion effect of imidazoline complexes on mild steel in CO₂-saturated solution was studied by LPR (Linear Polarization Resistance) corrosion rate. Figure 2 shows that, change in Corrosion Rate (CR) with time for carbon steel in CO₂-saturated 1% NaCl solution containing imidazoline complexes at 50 °C. The inhibitor was added after 1 hour of exposure because at this time the corrosion potential got stable, allowing the measurement of the corrosion rate prior the injection of the inhibitor.
Figure 1. IR Spectrum of the N-4 Complex

Figure 2. Variation of the Corrosion Rate with Time for Mild Steel in CO2-Saturated Brine Containing 100 ppm of Imidazoline Complexes at 50 °C

Table 3. The Corrosion Parameters for Mild Steel Electrode in 1% Solution of NaCl Saturated with CO2 in the Absence and Presence of 100 ppm of Different Imidazoline Complexes at 50 °C

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$I_{corr}$ (mA/cm²)</th>
<th>Corrosion Rate (mm/year)</th>
<th>Total Metal Loss (mg)</th>
<th>The Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.326548</td>
<td>3.7846</td>
<td>0.007461</td>
<td>-</td>
</tr>
<tr>
<td>N-1</td>
<td>0.002774</td>
<td>0.032147</td>
<td>0.000448</td>
<td>99.1</td>
</tr>
<tr>
<td>N-2</td>
<td>0.006137</td>
<td>0.071132</td>
<td>0.000461</td>
<td>81.2</td>
</tr>
<tr>
<td>N-3</td>
<td>0.035733</td>
<td>0.0220</td>
<td>0.000126</td>
<td>99.4</td>
</tr>
<tr>
<td>N-4</td>
<td>0.00321</td>
<td>0.037201</td>
<td>0.000686</td>
<td>99.0</td>
</tr>
</tbody>
</table>

4. Conclusion

The following conclusions have been drawn from the present study:

1. LPR corrosion rate was used to study the corrosion inhibition of mild steel in 1% NaCl solution saturated with CO2 using environmental friendly imidazoline complexes synthesized on the bases of naphthenic acid.

2. The structures of synthesized inhibitors were confirmed by physical-chemical spectroscopic methods.

3. All synthesized inhibitors showed inhibition characteristics for mild steel corrosion in 1% NaCl solution saturated with CO2.

4. The inhibition efficiency of synthesized inhibitors increased in the following order: N-3 > N-1 > N-4 > N-2.

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References


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