Full Length Research Paper

Investigation of Inorganic Complexes of Amidoamines Synthesized from Synthetic Oxy- and Petroleum Acids as Corrosion Inhibitor

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Abstract. Amidoamines have been synthesized based on the mixture of synthetic petroleum and oxy acids (SPA + OSPA) and polyethylene polyamine (PEPA). Physical and chemical indices of amidoamines have been identified. Complexes have been prepared from the amidoamine and HCl (Example 1), H₃PO₄ (Example 2), HNO₃ (Example 3) in ratio 1:1. The kinetic effect of steel corrosion in 1% NaCl solution saturated with CO₂ has been studied in ACM Gill AC potentiometer, at 50°C. Investigation was conducted at 25 and 50 ppm of each complex. It was found that, in Example 1 at 25 ppm after 20 hours of research the protection effect was 97.5%, at 50 ppm - 97.3%. In Example 2 at 25 and 50 ppm corrosion protection were 92% and 90.4% after 20 hours of research. In Example 3 at 25 and 50 ppm after 20 hours of research protective effects were 97.5 and 97.3%. It was determined that, amidoamine derivatives obtained from SPA + OSPA and PEPA, at 25 ppm was the best result-98.3%. By Calculated Gibbs free energy and the image of the surface of used electrode it has been proved that, a complex in different concentrates easily was exposed to chemisorption on metal surface. Therefore protective film formed on the surface was stable.

Keywords: Diesel fraction, synthetic petroleum acids, oxy acids, CO₂ corrosion, corrosion inhibitor, amidoamines

1. INTRODUCTION

The corrosion resistance of metals and alloys is a basic property interrelated to the easiness with which these materials react with a given environment. Corrosion is a natural process that seeks to reduce the binding energy in metals. The result of corrosion process involves oxidizing of metal atoms, whereby it loses one or more electrons and leaves the bulk metal. One of the main problems we have encountered in our industrialized society is metallic corrosion (Fang, 2007; Kermani, 1996). This process is consisting of three elements: an anode, a cathode and an electrolyte. The anode is the site of the corroding metal, the electrolyte is the corrosive medium that enables the transfer of electrons from the anode to the cathode, and the cathode forms the electrical conductor in the cell that is not consumed in the corrosion process (Zhao, 2009). In the oil and gas fields and pipelines, carbon dioxide (CO₂), hydrogen sulfide (H₂S), and free water are highly corrosive media (Hausler, 1984). It has been given much attention to carbon dioxide (CO₂) corrosion of carbon steel pipelines and equipment in the oil and gas industry in recent years. Because of an increased tendency to inject CO₂ into oil wells to reduce the viscosity of oil and increase its production (Ismayilov, 2012; Abbasov, 2013b).

There are various methods to hinder destruction or degradation of metal surface. The corrosion inhibitor is one of the best known methods of corrosion protection and one of the most useful on the industry. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film (Abbasov, 2013a; Abdel-Gaber, 2011; Yıldırım, 2008). Inhibitors have great acceptance in the industries due to excellent anti-corrosive properties.

The largest consumption of corrosion inhibitors is in the oil industry, particularly in the petroleum refining industry. Among the inhibitors nitrogen-base materials and their derivatives have the great importance (Abbasov, 2013c; Shaker, 2011; Mursalov, 2015).

This article is about the synthesis of amidoamines based on the mixture of the synthetic petroleum and oxy acids and protective effect on CO₂ corrosion of these derivatives. The aim of work - the advent of a new inhibitors that has to match up the above mentioned requirement, describe the mechanism of
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inhibitors’ action, main characteristics and the high efficiency on CO₂-corrosion.

2. MATERIALS AND METHODS

The mix of synthetic and oxy synthetic petroleum acids (SPA + OSPA) in the synthesis of a high efficient corrosion inhibitor was used. The mixture of SPA + OSPA was synthesized of the catalytic oxidation of naphthenic-paraffinic hydrocarbons separated from the diesel fraction of Azerbaijan oils. The process was realized for 6 hours in the temperature of 135°C in a sparging reactor (Abbasov, 2015b; Abbasov, 2014).

Amidoamines were synthesized on the based of the SPA + OSPA and polyethylene polyamine (PEPA) (Abbasov, 2013c). Condensation of the SPA + OSPA and PEPA was carried out at 130-140°C:

\[
\text{R-CH-CH}_2^\cdot \text{C-} \overset{\text{O}}{\text{OH}} + \text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{R-CH-CH}_2^\cdot \overset{\text{O}}{\text{NH}}(\text{CH}_2\text{CH}_2\text{NH})_n\text{CH}_2\text{CH}_2\text{NH}_2 - \text{H}_2\text{O}
\]

Some physical and chemical indices of synthesized amidoamines were presented in the Table 1.

<table>
<thead>
<tr>
<th>№</th>
<th>Indicators</th>
<th>Amidoamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aggregate state</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>2</td>
<td>Smell</td>
<td>Sharp</td>
</tr>
<tr>
<td>3</td>
<td>Colour</td>
<td>Dark brown</td>
</tr>
<tr>
<td>4</td>
<td>Molecular weight</td>
<td>542</td>
</tr>
<tr>
<td>5</td>
<td>Freezing temperature, °C</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Density, g/sm³; 20°C</td>
<td>1.1257</td>
</tr>
</tbody>
</table>

Fig. 1: IR spectrum of the HNO₃ complex of amidoamines

Complexes were prepared from the amidoamines and HCl (example 1), H₃PO₄ (example 2), HNO₃ (example 3) in ratio 1:1. Complexes based on amidoamines and HX (X = Cl, PO₄³⁻, NO₃⁻) were prepared in normal condition (Abbasov, 2015a; Afandiyeva, 2015a).

IR-spectrum of HNO₃ complex of amidoamines was taken on universal IR-spectrometer “ALPHA” (company BRUKER, Germany) using KBr disks in the vibration range 4000-500 cm⁻¹. IR-spectrum of complex is presented in Figure 1.

It is clear from the Figure 1 that, on 718 sm⁻¹ vibration of C-H bond of CH₂ group, on 1007 sm⁻¹, 1040 sm⁻¹ C-O bond of alcohol; on 1329 sm⁻¹ valence vibration of C-N bond; on 1641 sm⁻¹ C=O bond of
group of secondary amide; on 1455, 2854, 2923 sm⁻¹ deformation and valence vibration of C-H bond of CH₂ and CH₃ groups, on 3079, 3292 sm⁻¹ the N-H bond of secondary amide, on 2431, 2102 sm⁻¹ NH₃⁺ group of complex, on 1546 sm⁻¹ N-H bond of NH group.

The kinetic effects of steel corrosion in 1% NaCl solution saturated with CO₂ were studied in ACM Gill AC potentiometer (Song, 2004). The potential of the working electrode was varied by a CoreRunning programme (Version 5.1.4.) through an ACM Instrument Gill AC. A cylindrical carbon steel rod of the composition C1018 GRADE STEEL was used as a working electrode. 1% NaCl solution was prepared by dissolving of analytical grade NaCl in distilled water. The concentration range of the prepared surfactants was used 25, 50 ppm for corrosion measurements.

3. RESULTS AND DISCUSSIONS

The HCl, H₃PO₄, HNO₃ complexes of amidoamines at concentrations 25 and 50 ppm for 20 hours have been investigated. The Figures 2, 3, 4 show the effect of HCl, H₃PO₄, HNO₃ complexes of amidoamines on the corrosion rate of carbon steel in CO₂ saturated 1% NaCl solution from time at 50°C.

In Example 1 (Figure 2) at 25 ppm concentration after 20 hours of research the protection effect is 97.5%, at 50 ppm is 97.3%. In Example 2 (Figure 3) at 25 ppm and 50 ppm corrosion protection are 92% and 90.4% after 20 hours of research. In Example 3 at 25 ppm and 50 ppm after 20 hours of research protective effects are 97.4% and 97.3%.

Corrosion protection efficiency and thermodynamic parameters for the adsorption of all examples in 1% solution of NaCl, saturated with CO₂ are presented in Table 2.

As we can see from the Table 2, the kinetic effect of steel corrosion in 1% NaCl solution saturated with CO₂ for each example at 25 ppm concentration show the best results – 97.5% (ex.1), 92% (ex.2), 97.4% (ex.3). With increasing concentration up to 50 ppm, to further reduce the corrosion rate of carbon steel is observed (97.3%; 90.4% and 97.3%). The protective effect in Examples 1 and 3 are roughly the same (97.5% and 97.4%) at 25 ppm concentration. But the protective effect of Example 2 is lower (92%). It is related to the structure of the complex. Braking effect of reagents synthesized based on SPA + OSPA and PEPA may be due to the presence of O- and N-heteroatoms in the system, increasing the number of active centers, as well as the electron density and molecular size, accordingly, the intensity of precipitation of carbonates on the metal surface. Solution of synthesized amidoamines due free electron pairs of the nitrogen atoms in their composition, exposed chemisorption by surface of the metal. The amidoamine molecule forms a complex with inorganic acids. In consequence NH₃⁺ ions forms in the system.
Table 2: Corrosion protection efficiency and thermodynamic parameters for the adsorption of example 1, 2 and 3 in 1% solution of NaCl, saturated with CO₂

<table>
<thead>
<tr>
<th>Concentration, ppm</th>
<th>The braking effect, γ</th>
<th>Metal loss, mg</th>
<th>Protection effect, %</th>
<th>(K_{ads}), M⁻¹×10⁴</th>
<th>The surface coverage, θ</th>
<th>Gibbs energy, (\Delta G_{ads}) kJ/mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>31.2</td>
<td>0.000607</td>
<td>97.5</td>
<td>69.9</td>
<td>0.968</td>
<td>-43.0</td>
</tr>
<tr>
<td>50</td>
<td>21.4</td>
<td>0.000708</td>
<td>97.3</td>
<td>23.6</td>
<td>0.953</td>
<td>-40.6</td>
</tr>
<tr>
<td>Example 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>11.4</td>
<td>0.001024</td>
<td>92</td>
<td>24</td>
<td>0.913</td>
<td>-40.6</td>
</tr>
<tr>
<td>50</td>
<td>10.4</td>
<td>0.000667</td>
<td>90.4</td>
<td>13.4</td>
<td>0.904</td>
<td>-39.2</td>
</tr>
<tr>
<td>Example 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>38.1</td>
<td>0.000712</td>
<td>97.4</td>
<td>93</td>
<td>0.975</td>
<td>-44</td>
</tr>
<tr>
<td>50</td>
<td>38.1</td>
<td>0.000631</td>
<td>97.3</td>
<td>43.4</td>
<td>0.973</td>
<td>-42</td>
</tr>
<tr>
<td>Example 3</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Fig. 4: Corrosion rate-time curves for mild steel in CO₂-saturated 1% NaCl solution containing different concentrations of HNO₃ (S-6) complex of amidoamines at 50 °C

The acceleration of the anodic dissolution of iron take place in the aerobic acidic environment containing NaCl. With the addition inhibitor chemisorption of NH₃⁺ ion complex occurs to these parts. The obtained film is more durable, thereby protection of corrosion is better.

The mechanism of corrosion inhibition may be explained on the basis of the adsorption behavior of the inhibitors (Afandiyeva, 2015 b). The values of \(K_{ads}\) obtained from the Langmuir adsorption isotherm are listed in Table 2, together with the values of the Gibbs free energy of adsorption.

\[
\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \quad (I)
\]

\[
K_{ads} = \frac{1}{C_{inh}} \times \frac{\theta}{1-\theta} \quad (II)
\]

\[
\Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \quad (III)
\]

where \(K_{ads}\) is the equilibrium constant of the inhibitor adsorption process and \(C_{inh}\) is the surfactant concentration; \(R\) is the universal gas constant, \(T\) is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution.

It is known that, values of \(\Delta G_{ads}\) up to -20 kJ/mol⁻¹ are consistent with physisorption, while those around -40 kJ/mol⁻¹ or higher are associated with chemisorption as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond (Szklarska-Smialowska, 1978). From the table, we can see that, the values of the Gibbs energy for studied reagents between -39.2 and -44 kJ/mol⁻¹, which are less than -40 kJ/mol⁻¹ (Table 2). These results show that the adsorption mechanism of inorganic complexes of amidoamines on carbon steel in CO₂ saturated brine is typical chemisorption at the studied temperature. Thus, the
amidoamine complexes prevent disruption of metal by corrosion due forming a film on the metal surface.

IR spectra of used electrodes before and after corrosion on Example 3 and the image of their surface were taken on FT-IR microscopy LUMOS (company BRUKER, Germany) in the range of wave frequencies of 600-4000 cm\(^{-1}\).

The images of the surface of used electrode were selected 7 points and taken their IR spectra (Figure 5 and 6):

![Fig. 5: The image of surface of new (a) and the used electrode (b)](image)

Analysis of IR-spectrum of point 1 shows that, this spectrum generally belongs to complex of amine (713, 1428 sm\(^{-1}\) – C-H bond; 1557, 1644, 3247 sm\(^{-1}\) – N-H bond; 1117 sm\(^{-1}\) – O-H bond).

Comparing the IR-spectra of points 1 and 2 can be concluded that, they are almost identical. Note that, in the spectra the points 2, 3, 4, 5, 6 along with the absorption band on 1703 sm\(^{-1}\) appear several bands very weak intensity; on 1668-1800sm\(^{-1}\) is also characteristic of the C = O bond. The weak intensity of the absorption band of C=O bond confirmed that corrosion process of the surface of electrode happened slightly.

4. CONCLUSION

Corrosion of carbon steel in CO\(_2\)-saturated 1% NaCl solution and the inhibiting effect of the HCl, H\(_3\)PO\(_4\), HNO\(_3\), complexes of amidoamines synthesized based on SPA and nitrogen containing compounds have been studied. It has been found that, all studied compounds act as effective inhibitors in the investigated medium. The results proved that, for each example at 25 ppm concentration show the best result – 97.5% (Ex.1), 92% (Ex.2), 97.4% (Ex.3). The Gibbs energy for studied reagents between -39.2 and -44 kJ/mol\(^{-1}\), which are less than -40 kJ/mol\(^{-1}\). Calculated Gibbs free energy of adsorption confirms that the adsorption process takes place spontaneously. Analysis of IR-spectra of points showed that, this spectrum generally belongs to complex of amine. Thus, we can say that, complexes in different concentrates easily exposed to chemisorption on metal surface, and protective film which is formed on the surface is stable.
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