Green surfactants from the type of fatty acids as effective corrosion inhibitors for mild steel in CO$_2$-saturated NaCl solution

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Abstract: Four sulfated fatty acid diethanolamine complexes (DC) were synthesized based on four different types of vegetable oils and tested as corrosion inhibitors of mild steel in CO$_2$-saturated 1% NaCl solution at 50 °C. Results obtained show that the surfactants studied are efficient corrosion inhibitors for mild steel even at low concentrations. It is found that the inhibition efficiency increases with the concentration, and the good inhibition efficiencies are reached near their critical micelle concentrations (99.95% at 100 ppm). The adsorption of inhibitor on the steel surface obeys the Langmuir adsorption isotherm equation and was chemisorption. Energy dispersive X-ray fluorescence microscopy (EDRF) observations of the electrode surface confirmed the existence of such an adsorbed film.

Keywords: Steel, Vegetable oils, Corrosion Inhibitor, Surfactants, EDRF

1. Introduction

Dissolved CO$_2$ in aqueous solutions can lead to serious corrosion on the steel pipelines or equipments used in the oil/gas production or transport, which can even result in major safety accident [1, 2]. The understanding of CO$_2$ corrosion mechanisms under the effects of many mechanical and environmental factors, such as flow, temperature, pressure, oil–water ratio, pH, solution chemistry, and corrosion product layer, has been of great concern in corrosion field [3–5]. Carbon steels are often used as materials in oil-producing and -gathering facilities; however, they are very susceptible to corrosion in CO$_2$ environments, leading to severe damage.

The use of chemical inhibitors has been acknowledged as one, and a very practical and most economical, method of combating CO$_2$ corrosion [6]. An important corrosion inhibition tool is the use of surfactant inhibitors. The most important action of inhibition is the adsorption of the surfactant functional group onto the metal surface [7], adsorption is critical to corrosion inhibition. The ability of a surfactant molecule to adsorb is generally related to its ability to aggregate to form micelles. Most acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms [8, 9]. Inhibition of metal corrosion by surfactant compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal.

Surfactant inhibitors have many advantages, for example, high inhibition efficiency, low price, low toxicity, and easy production [10, 11]. Moreover, the investigation of surfactants adsorbed on metal surfaces is extremely important in electrochemical studies such as corrosion inhibition, adhesion, lubrication, and detergency [12]. The effective type of corrosion inhibitors for these applications is film-forming inhibitors. The inhibition of steel corrosion using different types of surfactants has been investigated by many workers [13, 14].

The paper aims to investigation of the effectiveness of the new synthesized, environmental friendly surfactants from the type of fatty acids (sulfated fatty acid diethanolamine complexes; Fig.1) on the corrosion rate of mild steel in CO$_2$-saturated 1% NaCl solution and to identify the adsorption isotherm that most describes the behavior of the
inhibitor molecules on the metal surface.

Figure 1. Molecular structure of sulfated fatty acid diethanolamine complex (DC).

2. Material and Methods

2.1. Chemical Composition of the Investigated Mild Steel Alloy C1018

Electrodes are made of steel grade 080A15 and have an area of 4.55 cm$^2$ (rotating cylinder electrode). These electrodes are used for one time. The mechanical properties of the mild steel measured at room temperature were provided by supplier as follows: tensile strength equal to 490 MPa and elongation to failure equal to 16%. The Chemical composition of mild steel used in this study was given in Table 1. The data was provided by European Corrosion Supplies Ltd.

2.2. Synthesis of Complex Surfactants

The complex surfactant used as inhibitor is sulfated fatty acid-diethanolamine complex (DC). The inhibitors were synthesized in our laboratory based on different four types of vegetable oils (DC$_I$ based on sunflower oil, DC$_{II}$ based on cottonseed oil, DC$_{III}$ based on corn oil and DC$_{IV}$ based on palm oil). The oil was hydrolyzed with solution of 25% NaOH for 7 hours at 90 °C. This process yield in fatty acid sodium salt which is reacted with 37% HCl acid solution for extracting the fatty acids. Based on prepared fatty acid the sulfating syntheses were performed. The product is Sulfated fatty acid. The product was characterized by FT-IR spectroscopy (using a model FT-IR, Spectrum BX spectrometer using KBr disks). Sulfated fatty acid was taken at molar ratio 1:2 with diethanolamine. The components of reactions were mixed well for a period 60 min at 25 °C. The chemical structure of the synthesized complex surfactant was characterized by using physical chemical methods (Table 2) and FT-IR, Spectrum BX spectrometer using KBr disks.

Table 1. Chemical composition of mild steel C1018 alloy.

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>S</th>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, (wt. %)</td>
<td>0.37</td>
<td>0.01</td>
<td>0.07</td>
<td>0.03</td>
<td>0.18</td>
<td>0.03</td>
<td>0.71</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 2. Physical and chemical properties of fatty acid and sulfated fatty acid synthesized based on the investigated oils.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Obtaining acid</th>
<th>Acid number mg KOH/g</th>
<th>Molecular weight g/mol</th>
<th>Iodine number 100 g iodine / g of sample</th>
<th>Density, kg/m$^3$</th>
<th>Refraction, $\eta_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sunflower</td>
<td>Fatty acid</td>
<td>145.6</td>
<td>279</td>
<td>112</td>
<td>907.5</td>
<td>1.4680</td>
</tr>
<tr>
<td></td>
<td>Sulfated fatty acid</td>
<td>280</td>
<td>377</td>
<td>----</td>
<td>901.1</td>
<td>1.4610</td>
</tr>
<tr>
<td></td>
<td>Fatty acid</td>
<td>142.5</td>
<td>275</td>
<td>115</td>
<td>911</td>
<td>1.4670</td>
</tr>
<tr>
<td>cottonseed</td>
<td>Sulfated fatty acid</td>
<td>269</td>
<td>373</td>
<td>----</td>
<td>917</td>
<td>1.4590</td>
</tr>
<tr>
<td>corn</td>
<td>Fatty acid</td>
<td>147.5</td>
<td>278</td>
<td>103</td>
<td>910</td>
<td>1.4660</td>
</tr>
<tr>
<td></td>
<td>Sulfated fatty acid</td>
<td>284</td>
<td>376</td>
<td>----</td>
<td>915</td>
<td>1.4580</td>
</tr>
<tr>
<td></td>
<td>Fatty acid</td>
<td>155.8</td>
<td>269</td>
<td>43</td>
<td>901.7</td>
<td>1.4644</td>
</tr>
<tr>
<td>palm</td>
<td>Sulfated fatty acid</td>
<td>294</td>
<td>367</td>
<td>----</td>
<td>917</td>
<td>1.4571</td>
</tr>
</tbody>
</table>
2.3. Corrosion Inhibition Test

The aggressive solution, 1% NaCl, was prepared by dissolving of analytical grade NaCl in distilled water. The concentration range of the prepared inhibitors was from 10 to 100 ppm used for corrosion measurements.

2.4. Corrosion Measurements

To study the corrosion protection ability of the synthesized surfactants, one of the newest devices in recent years ACM, GILL AC was used. The apparatus consists of a personal computer HP Pavilion (monitor, CPU), a Potentiostat/Galvanostat model ACM GILL AC (UK), four pieces of glasses with a capacity of 4000 ml, electrodes, CO_{2} tank and installations-regulating the quantity fed CO_{2}. A magnetic stirrer stirred the prepared 1% of the sodium chloride solution for 30 minutes in a 4 L beaker. The prepared solution poured into the four glass beakers (1000 ml for each one). These beakers were, then placed on a heater at 50 °C for 1 hour under a pressure of 0.9 bar carbon dioxide saturated the solution. The electrodes were immersed in the medium and are connected through a potentiometer ACM GILL AC. The surfaces of working electrode were cleaned by acetone before using. Electrodes are used for one time only. After 1 hour, except for one beaker, the remaining three were fed with the suitable amount of inhibitor and continued supply of CO_{2} under 0.9 bar pressure till the end of the experiment.

A Core Running program (Version 5.1.3.) varied the potential of the working electrode through a potentiometer ACM instruments Gill AC. Gill AC technology allows measuring DC and AC signals using standard Sequencer software. A small sweep from typically, -10 mV to +10 mV, at 10 mV min-1 around the rest potential is performed. The Core Running program converts a corrosion current in mA cm⁻² to different relationships (building on the corrosion rate per time (mm year⁻¹), the metal loss per time (mg h⁻¹).

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.

2.5. Surface Tension Measurements

The surface tensions were determined by DuNoüy Tensiometer, Kruss Type 8451 and the temperature was maintained precisely at 25 °C. Critical micelle concentration (CMC) values of surfactants were determined, according to the break points in plots of the surface tension versus log molar concentration of investigated surfactants.

2.6. Surface Characterization

In order to observe any changes in surface morphologies of the mild steel samples after testing, the specimens were first immersed in the test media with and without an inhibitor for 5 days, then cleaned with bi-distilled water and acetone, and dried with cool air. Then the morphology of the tested sample was observed by using HORIBA XGT-7000 - Energy dispersive X-ray fluorescence (EDRF), a microscope with a system of partial / complete evacuation of the sample.

3. Results and Discussion

3.1. Chemical Structure of the Synthesized Surfactants

Physical and chemical properties of fatty acid and sulfated fatty acid synthesized based on corn oil were studied and listed in Table 2. The data showed that, the acid number is increased and no reaction with iodine after sulfating process. These results confirmed that, the complete removal of C=O bond by sulfating process and formation of sulfated fatty acid.

The chemical structures for purified product (DC complex) were recorded in FT-IR. The FT-IR absorption spectra showed an absorption band at the 2330-2348 cm⁻¹ region for the prepared surfactant, indicating that the amine band was disappearing by forming amide group (-HN-C=O). In addition, there was a strong band at 851-902 cm⁻¹, indicating the presence of multiple (CH₃) groups. The very strong bands at the 2843-2862 cm⁻¹ region for the prepared compound were due mainly to the methyl asymmetric stretching vibration. The sharp band at 2919-2960 cm⁻¹ was observed for all purified surfactants due to the stretching vibration of the symmetric methylene group. The strong band at 1715-1730 cm⁻¹ for all compounds indicating to the increasing C=O group frequency due to occurring a link between the acid proton with the amino nitrogen that leads to increasing the attraction of electrons from carbonyl group. The peak at 1375 cm⁻¹ is due to S-O stretching absorption bands. The FT-IR absorption spectra confirmed that the disappearance of -OH band of acid in sulfated fatty acid.

3.2. Corrosion Inhibition Measurements and Adsorption Isotherm

The synthesized inhibitors were tested with linear polarization-resistance corrosion rate (LPR) and rotating- cylinder-electrode (RCE) techniques. In all cases, tests were performed on mild steel under CO_{2}-saturated 1% NaCl solution. The bubble-test method involves evaluating the corrosion of a given metal in simulated brine saturated with CO_{2} at a temperature equivalent to that in the field. During the test, CO_{2} gas is sparged continuously into the test solution. The rate of corrosion is determined instantaneously with the LPR technique.

Figure 2 shows that, the change in corrosion rate (CR) with time for mild steel in CO_{2}-saturated 1%NaCl solution containing different concentrations form inhibitor DC_{100} 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 CR prior the injection of the inhibitor. The initial corrosion rate, without inhibitor, was measured to be between 2.59 and 3.784 mm y⁻¹. It was found from Figure 2 the corrosion rate, in the absence of inhibitor, tends to increase with time. The increase in CR has been attributed to the galvanic effect between the ferrite phase and cementite (Fe₃C) which is a part of the original steel in the non-oxidized state and accumulates on the surface after the preferential dissolution of ferrite (α-Fe) into Fe²⁺ [15]. Fe₃C is known to be less active than the ferrite phase. Therefore, there is a preferential dissolution of ferrite over cementite, working the former as the anode and latter as the cathode, favoring the hydrogen evolved reaction (HER) during the corrosion process [16, 17].

![Inhibitor addition](image1)

**Figure 2.** Variation of the Corrosion rate with time for mild steel in CO₂-saturated 1 % NaCl solution containing different concentrations of inhibitor DCIII complex at 50 °C.

The corrosion parameters were calculated on the basis of LPR corrosion rate test. The inhibition efficiency (η %) was calculated according to the following equation.

\[
\eta\% = \frac{CR_o - CR_i}{CR_o} \times 100
\]  

(1)

where CRo is the corrosion rate without inhibitor and CRi is the corrosion rate when inhibitor is present. The obtained experimental results show that, the addition of the under testing surfactants greatly decreases the corrosion rate of mild steel in the given aggressive media, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency 99.95 % at 100 ppm after 20 hour of exposure for DCIII (Table 3). This trend may results from the fact that adsorption and surface coverage increase with the increase in concentration; thus the surface is efficiently separated from the medium [18].

Table 3 shows the calculated values of corrosion rates, the inhibition efficiencies and the surface coverage in the absence and presence of different concentrations of different inhibitors at 50 °C. The data exhibited that, the corrosion rates, the inhibition efficiencies and the surface coverage are found to depend on the concentrations of the inhibitors. The corrosion rate (CR) are decreased, and the inhibition efficiencies (η %) and the surface coverage (θ) are increased with the increase of the surfactant concentrations. This indicates that the inhibitory action of the inhibitors against mild steel corrosion can be attributed to the adsorption of these molecules on the metal surface, limits the dissolution of mild steel, and the adsorption amounts of surfactants on mild steel increase with concentrations in the corrosive solutions. This ability of formation of protective surface layers increases with the increase of surfactant concentration.

Table 3. The corrosion parameters obtained from LPR corrosion rate measurements for mild steel electrode in CO₂-saturated 1% solution of NaCl in the absence and presence of various concentrations of DC complexes obtained based on vegetable oils at 50 °C.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Concentration, ppm</th>
<th>Corrosion rate (mm/year)</th>
<th>Surface coverage, θ</th>
<th>The inhibition efficiency, η%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0</td>
<td>3.784</td>
<td>-----</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.585</td>
<td>0.845</td>
<td>84.52</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.218</td>
<td>0.942</td>
<td>94.20</td>
</tr>
<tr>
<td>DC III</td>
<td>50</td>
<td>0.102</td>
<td>0.973</td>
<td>97.30</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.048</td>
<td>0.987</td>
<td>98.71</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.027</td>
<td>0.992</td>
<td>99.28</td>
</tr>
<tr>
<td>DC IV</td>
<td>10</td>
<td>0.517</td>
<td>0.8632</td>
<td>86.32</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.392</td>
<td>0.8962</td>
<td>89.62</td>
</tr>
</tbody>
</table>
The results also show that, the inhibition efficiencies in the case of surfactant complex obtained on the basis of corn oil are higher compared with those of inhibitors obtained based on other oils at the same conditions (Fig. 3), and the results showed the following trend at 100 ppm of different inhibitors.

\[ \text{DC}_{III} > \text{DC}_{II} > \text{DC}_{I} > \text{DC}_{IV} \]

This behavior may be due to the difference in fatty acids compositions of the investigated oils. The fatty acid composition of oils from vegetable sources varies depending on plant origin and sort [19]. The inhibition efficiency values of inhibitors depend on the molecular weight. The η% values of inhibitor DCIII are higher than those of other inhibitors, due to the larger molecular weight of the former compared with that of the latter.

Figure 3 shows the variation of the corrosion rate with time for mild steel in CO\(_2\)-saturated 1% NaCl solution containing 100 ppm from DC complex based on all oils at 50 °C. This plot indicates that, the presence of different inhibitors decreases the rate of corrosion. However, the maximum decrease in the corrosion rate was observed for inhibitor DCIII. The highest inhibition efficiency of the investigated inhibitors may be attributed to the following reasons.

The higher electron density on the functional groups (N, O and S) leads to easier bond formation, greater ad sorption, and consequently, higher inhibition.

Figure 3. Variation of the Corrosion rate with time for mild steel in CO\(_2\)-saturated 1% NaCl solution containing 100 ppm of DC based on all investigated oils at 50 °C.

The adsorption of synthesized surfactants on the metal surface can occur either directly on the basis of donor-acceptor interactions between the oxygen or sulfur groups and the vacant d-orbitals of steel surface atoms or an interaction of organic nitrogen compounds with already adsorbed groups.

There was an increase in the efficiency of corrosion inhibition with increasing concentration, since the adsorption of C=O, oxygen, nitrogen and sulfur groups onto the metal surface was stronger, and effectively protecting the surface. Conclusively, the surfactant inhibitor, having near unity θ (see Table 3), was considered as a good physical barrier shielding the corroding surface from corrosive medium and dumping the corrosion rate of mild steel significantly.

The high inhibition efficiency obtained in CO\(_2\) -saturated NaCl solution in the presence of studied complex surfac-
tants by the investigated method can be attributed to the formation of a protective film of iron carbonate (FeCO₃) as follows [21].

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \quad (2)
\]

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(aq) \quad (3)
\]

\[
\text{H}_2\text{CO}_3(aq) \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (4)
\]

\[
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (5)
\]

The anodic dissolution for iron in carbonic acid solutions gives ferrous ions [21].

\[
\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (6)
\]

According to these processes, a corrosion layer was formed on the steel surface. The properties of the formed layers and its effect on the corrosion rate are important factors to take into account when studying the corrosion of steels in CO₂ environments. Ogundele and White suggested that, iron carbonate, FeCO₃, may be important in the formation of protective layers on steel surface [22]. The formation of iron carbonate can be explained by using the following Eq.[23].

\[
\text{Fe}^{2+} + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3 \quad (7)
\]

In order to get more information about the mode of adsorption of the complex surfactants on the surface of the investigated metal at 50 °C, the data obtained from LPR corrosion rate have been tested with several adsorption isotherms. Langmuir adsorption isotherms were found to fit well with the experimental data. It is generally accepted that the values of \( \Delta G_{ads}^o \) around -20 kJ/mol or less is assumed for electrostatic interactions exist between inhibitor and the charged metal surface (physisorption) [24]. Values of -40 kJ/mol or more indicate charge transferring from organic specie to the metal surface, to form a coordinate type of metal bond (Chemisorption) [25]. It is clear that, the values of the standard free energy of adsorption \( \Delta G_{ads}^o \), in our measurements are ranged between -42.18 and -47.31 kJ/mol, which suggests the adsorption of inhibitor molecules onto the metal surface as chemisorption. Chemisorption of the surfactant molecules could occur due to the formation of links between the d orbital of iron atoms, involving the displacement of water molecules from the metal surface, and the lone sp2 electron pairs present on the N, S and/or O atoms of the inhibitor.

3.3. Surface Tension Measurements

It is well known that surfactants are characterized by critical micelle concentration (CMC). The CMC is the concentration where surfactants in solution change their initial molecular solvated state [26]. At this concentration, physical and chemical properties exhibit an abrupt variation. CMC values often exhibit a weak dependence on tempera-

ture. In order to determine the CMC of the investigated complex surfactants, the surface tension (\( \gamma \)) of various concentrations of the surfactant was measured at 25 °C. The relation between \( \gamma \) and concentration is shown in Fig. 4. The intercept of the two lines indicates the CMC. It can be seen that the critical micelle concentration of synthesized surfactants are ranged from \( 4.1 \times 10^{-4} \) to \( 5 \times 10^{-4} \) mol/l approximately. It is observed that, the highest inhibition efficiencies are observed when the surfactant concentration reaches values close to its critical micellar concentration (CMC). As the concentration of surfactant molecules approaches the CMC, micelles form in solution, and similar aggregate structures such as bilayers and multilayers form on the surface (see Figure 4). Further increase in surfactant concentration above the CMC results in other types of aggregates such as lamellar structures and rod-like micelles that can form in solution as well as analogous bilayers or multilayers that form at interfaces [27, 28].

![Figure 4. Change of surface tension (\( \gamma \)) with the concentration of the surfactants at 298 K](image)

3.4. Surface Characterization

Fig. 5a shows an EDRF spectroscopy for mild steel surface in CO₂-saturated 1% NaCl solution without inhibitors. The characteristics peaks are related to Fe, Mn, P, Cr and oxygen elements. This indicated that the corrosion product on mild steel surface being metal oxide. However, the data in Fig. 6a in the presence of 100 ppm of inhibitor DC III shows additional peaks characteristic of N element, and the lower peaks height of Fe than those observed in the absence of inhibitors. This result proved that the adsorption of inhibitor molecule on mild steel surface leads to a decrease of metal oxide layer, and higher concentration of the inhibi-
tor is necessary to delay the corrosion process.

Figures 5b, 6b show the picture of the passive film formed on the mild steel surface after immersion in CO₂-saturated brine for 5 days in the absence and presence of inhibitor DC III. In the absence of inhibitor (Fig. 5b), the results exhibited that thick porous layer of corrosion prod-
uct (oxide film and FeCO₃) covered all electrode surface; the surface was strongly damaged, so that the electrode surface can not be seen. While Fig. 6b shows the image of the electrode surface in presence of 100 ppm of the investigated inhibitor. The image reveal that, the surface is almost free from damages and it is smooth, which indicates a good protective film present on the mild steel surface and also confirms the highest inhibition efficiency of the prepared complex surfactants.

![Figure 5. EDRF analysis of mild steel electrode surface after immersion in CO₂-saturated solution for 5 days without inhibitor (a) and the picture at the same conditions (b).](image)

![Figure 6. EDRF analysis of mild steel electrode surface after immersion in CO₂-saturated solution containing 100 ppm inhibitor DCIII for 5 days (a) and the picture at the same conditions (b).](image)

### 4. Conclusion

Sulfated fatty acids diethanolamine acts as a good inhibitor for the corrosion of steel in CO₂-saturated 1% NaCl solution, and the maximum inhibition efficiency is about 99.95% in the presence of 100 ppm of the complex obtained based on corn oil. The inhibition efficiency values increase with the inhibitor dose. The observed corrosion data indicate that, the inhibition of mild steel corrosion is due to the adsorption of the inhibitor molecules on the surface, which follow Langmuir adsorption isotherm. Energy dispersive X-ray fluorescence microscopy observations of the electrode surface showed that a surface film of inhibitor is formed on the electrode surface.
References


