Synthesis and Characterization of new Ethoxylated Carbohydrate based Surfactants for Corrosion Inhibition of low LCS Steel in Aqueous Solutions

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Abstract: The heterocyclic compounds, mainly carbohydrate-based surfactant, 1, 4 Sorbitan, namely (Sorbitan Mono-stearate with 20 moles of Ethylene oxide SMS-20-EO, Sorbitan Mono-oleate SMO, and Sorbitan Mono-oleate ethoxylated with 20 moles of Ethylene oxide SMO-20-EO) have been synthesized and characterized through different spectroscopic methods (FTIR, ¹H NMR). Then estimated as corrosion inhibitors of low LCS (LCS) in the aggressive environment 1 M HCl utilizing a weight loss (WL), the destructive and destructive electrochemical techniques. The surface examination was tested using several techniques. The new ethoxylated carbohydrate-based surfactant gave an excellent inhibition performance (IE %). The adsorption of the inhibitors obeys the Langmuir adsorption model. The metal dissolution and inhibitor adsorption phenomena have been studied via the estimation of thermodynamic parameters, which describe the adsorption properties of SMO, SMO-20-EO, and SMS-20-EO.

Keywords: Synthesis; Characterization; Corrosion inhibition; Low LCS; HCl and Carbohydrate based surfactant.

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1. Introduction

The advantages of using surfactants as corrosion inhibitors are due to they yield high inhibition efficiency [1], easily produced in a large scale, low toxicity, and low price [2]. Predominantly, the inhibitory action of surfactant molecules in aqueous solution may be attributed to chemisorption or electrostatic physical adsorption onto the metallic surface [3]. The development of surfactants based on natural renewable resources is a concept that is gaining recognition from different industries [5, 6]. Carbohydrate-based surfactants are the final result of a product concept that is based on the greatest possible use of renewable resources. Whereas the derivatization of fats and oils to produce a variety of different surfactants for a broad range of applications has a long tradition and is well established, the production of surfactants based on fats, oils, and carbohydrates on a larger industrial scale is relatively new [7, 8]. The structure of a typical surfactant with a hydrophilic head group and a hydrophobic tail always attach a carbohydrate molecule as a perfect polar head. Due to its
many hydroxyl groups, in fat and oil derivatives [9, 10]. Sugar surfactants have several rather flexible properties. A class of carbohydrate-derived surfactants, called sorbitan esters (anhydrous sorbitol), is derived from sorbitol, a hexitol produced by the catalytic reduction of glucose. In acidic conditions, sorbitol is dehydrated to sorbitan and even further to bicyclic isosorbide. Several authors have used surfactants as corrosion inhibitors for CS (LCS) and MS (mild steel) in HCl solution [11-22]. Sorbitan fatty acid ester surfactants can be produced by a direct or indirect industrial process (Fig. 1).

![Synthesis of sorbitan esters by intramolecular dehydration of sorbitol in the presence of acid at 150–200°C and subsequent base-catalyzed esterification with fatty acids at 200–250°C.](https://doi.org/10.33263/BRIAC112.93829404)

The aim of this paper is to synthesize and characterize some sorbitan fatty esters and ethoxylated sorbitan fatty esters as carbohydrate-based surfactants, and to calculate the inhibition efficiency of these surfactants for LCS corrosion in 1M HCl electrolytes by electrochemical, weight loss, and Surface analysis techniques.

2. Materials and Methods

The experiment was carried out with LCS with the following composition per weight % is shown in Table 1; rectangular specimens with dimensions 2 x 2 x 0.2 cm were used for WL measurements. For electrochemical tests, the exposed surface area of LCS was prepared as 1 cm².

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (Weight %)</td>
<td>0.14</td>
<td>0.1</td>
<td>0.01</td>
<td>0.024</td>
<td>0.5</td>
<td>0.05</td>
<td>0.05</td>
<td>Reset</td>
</tr>
</tbody>
</table>

2.1. Chemicals and solutions.

The investigated carbohydrate-based surfactant named Sorbitan Mono-stearate with 20 moles of Ethylene oxide SMS-20-EO, Sorbitan Mono-oleate SMO, and Sorbitan Mono-oleate ethoxylated with 20 moles of ethylene oxide SMO-20-EO. The new surfactants are easily soluble in methanol and dimethyl sulfoxide, which have high molecular weights, and contain many donating atoms. The aggressive electrolytes used were prepared from 37 % HCl. Appropriate Concentrations of acid was prepared using twice distilled water. Prepared concentrations of pervious new surfactants are 25, 50, 75, 100, and 125 ppm in 1 M HCl aggressive media. All the materials are AR grade.
2.2. Synthesis of carbohydrate-based surfactants.

2.2.1. Synthesis of sorbitan mono-oleate.

The synthesis is carried out in two steps:

Step 1 (Preparation of anhydrous sorbitol):

207.8 grams from Sorbitol 70% Aqueous Solution (D-Glucitol) and 2.6 grams of activated charcoal powder DARCO G 60 AR were charged into a round-bottom 500-mL 4-necked flask equipped with a reflux condenser, stainless steel stirrer, and 2 feed streams separated, vacuum gauge, Vacuum Pump. The evacuation of the reactor system was carried out to a pressure of about 6 mm of mercury and raising the temperature to 95°-100 °C in order to remove the water present in the sorbitol. 1.5 grams of p-toluene sulfonic acid catalyst will be charged to the reactor system after all the aqueous solvent was removed. The P-toluene sulfonic acid function is to allow the reaction to go to completion at a lower temperature. Then evacuating the reactor system is carried out again and then heating to 150°C. After the addition is complete, stirring is continued at a constant temperature for 130 minutes. Then, cooling of the reaction mixture was carried out, then, 0.35 gram of sodium hydroxide and 0.7 gram of Hyflosupercel diatomaceous earth Powder were added. Hyflosupercel was used as a filtration agent and also used as a clarifying agent. The reactants then were agitated for 20 minutes, and filtration at about 100°-120° C under an inert nitrogen atmosphere was carried through a sintered glass filter funnel (Scheme 1) [23-25].

![Scheme 1](image)

Scheme 1. The chemical synthesis pathway of anhydrosorbitol or 1,4-Sorbitan.

Step 2 (Preparation of sorbitan mono-oleate):

27.8 grams from Anhydro sorbitol that was prepared in the first step, 36.3 grams from commercial Industrene® 106 Oleic Acid supplied by Chemtura, 0.15 gram from powdered sodium hydroxide, and 0.9 gram of activated charcoal powder DARCO G 60 AR, were charged into a round-bottom 500-mL 4-necked flask equipped with a reflux condenser, stainless steel stirrer, and 2 feed streams separated. The reaction mixture was purged with inert nitrogen gas and then heating the reactants at atmospheric pressure to 205 ° C. for 45 minutes. Maintaining the reaction mixture at the predetermined temperature and pressure was carried out for 360 minutes while maintaining a slight flow of inert nitrogen gas. Cooling the reaction mixture was then carried out and was then left standing overnight. Heating of the reaction mixture in the next morning was then carried out to 105° C. while maintaining a slight flow of inert nitrogen gas, then treatment of the reaction mixture with 0.30 grams of 85% phosphoric acid for neutralization of the product and 0.30 gram of Hyflosupercel diatomaceous earth Powder. The reactants then were agitated for 20 minutes, and filtration at about 100°-120° C under an inert nitrogen atmosphere was carried through a sintered glass filter funnel [26].

Finally, the product (Scheme 2) was bleached with 0.5% (from the total weight of the product) Hyprox ™ 500, which is a 50% Aqueous solution of Hydrogen Peroxide, and then filtration for the product again is carried out in the presence of Hyflosupercel diatomaceous earth Powder.
Scheme 2. The chemical structure of the prepared Sorbitan Mono-oleate surfactant and is designated as SMO.

2.2.2. Synthesis of sorbitan monostearate.

The synthesis is carried out in two steps:

Step 1 (Preparation of anhydrous sorbitol):

207.8 grams from Sorbitol 70% Aqueous Solution (D-Glucitol) and 2.6 grams of activated charcoal powder DARCO G 60 AR were charged into a round-bottom 500-mL 4-necked flask equipped with a reflux condenser, stainless steel stirrer, and 2 feed streams separated, vacuum gauge, Vacuum Pump. The evacuation of the reactor system was carried out to a pressure of about 6 mm of mercury and raising the temperature to 95°-100 °C in order to remove the water present in the sorbitol. 1.5 grams of p-toluenesulfonic acid catalyst will be charged to the reactor system after all the aqueous solvent was removed. The P-toluene sulfonic acid function is to allow the reaction to go to completion at a lower temperature. Then evacuating the reactor system is carried out again and then heating to 150°C. After the addition is complete, stirring is continued at a constant temperature for 80 minutes. Then, cooling of the reaction mixture was carried out, then, 0.35 gram of sodium hydroxide and 0.7 gram of Hyflosupercel diatomaceous earth Powder were added. Hyflosupercel was used as a filtration agent and also used as a clarifying agent. The reactants then were agitated for 20 minutes, and filtration at about 100°-120° C under an inert nitrogen atmosphere was carried through a sintered glass filter funnel [27].

Step 2 (Preparation of sorbitan monostearate):

64.8 grams from Anhydro sorbitol that was prepared in the first step, 144.2 grams from commercial Industrene® 9018 FG Stearic Acid, 0.5 gram from powdered sodium hydroxide, and 1.9 grams of A fine black decolorizing Activated charcoal powder DARCO G 60 AR, were charged into a round-bottom 500-mL 4-necked flask equipped with a reflux condenser, stainless steel stirrer, and 2 feed streams separated. The reaction mixture was purged with inert nitrogen gas and then heating the reactants at atmospheric pressure to 205 °C. For one hour. Maintaining the reaction mixture at the predetermined temperature and pressure was carried out for 240 minutes while maintaining a slight flow of inert nitrogen gas. Cooling the reaction mixture was then carried out and was then left standing overnight. Heating of the reaction mixture in the next morning was then carried out to 105° C. while maintaining a slight flow of inert nitrogen gas, then treatment of the reaction mixture with 0.80 grams of 85% phosphoric acid for neutralization of the product and 0.8 gram of Hyflosupercel diatomaceous earth Powder. The reactants then were agitated for 20 minutes, and filtration at about 100°-120° C under an inert nitrogen atmosphere was carried through a sintered glass filter funnel [28]. Finally, the product (Scheme 3) was bleached with 0.5% (from the total weight of the product) Hyprox™ 500, which is a 50% Aqueous solution of Hydrogen Peroxide, and then filtration for the product again is carried out in the presence of Hyflosupercel diatomaceous earth Powder.
Scheme 3. The chemical structure of the prepared Sorbitan Monostearate surfactant and is designated as SMS.

2.2.3. Ethoxylation of sorbitan monooleate and sorbitan monostearate surfactants.

The synthesis of Sorbitan Monooleate and Sorbitan Mono-stearate ethoxylated with 20 moles of Ethylene oxide gas was conducted in a 2-L autoclave as carried out in our previous publication [29]. The previously prepared Sorbitan Monooleate or Sorbitan Mono-stearate was charged into a high-pressure stainless steel autoclave with KOH (1.0 wt. %) as a catalyst at 130 °C with continuous stirring while passing a stream of nitrogen gas through the system for 10 min to flush out the air. The nitrogen stream was then closed and replaced by a molar ratio of 20 units of ethylene oxide (EO) gas. The reaction completion was accepted when the pressure reached its minimum value. At this stage, heating was stopped, and the vessel contents were cooled. After cooling, the product obtained was neutralized with acetic acid. The yield was then collected. The obtained surfactants (Scheme 4, 5) appeared as a colorless viscous liquid appearance.

Scheme 4. The chemical structure of sorbitan monooleate ethoxylated with 20 moles of ethylene oxide and is designated as SMO-20-EO.

Scheme 5. The chemical structure of sorbitan monostearate ethoxylated with 20 moles of ethylene oxide and is designated as SMS-20-EO.

2.3. Characterization of the new ethoxylated carbohydrate-based surfactants.

2.3.1. Spectroscopic investigation of the prepared new ethoxylated carbohydrate-based surfactants.

The chemical structures of the prepared new Ethoxylated carbohydrate-based surfactants were confirmed by the FTIR and 1H NMR spectra. FTIR was carried out using the
Pye Unicam SP1200 spectrophotometer using the KBr Wafer technique in the region from 4000 to 500 Cm\(^{-1}\). \(^1\)H-NMR spectra were determined on BRUKER 400 MHZ (D- DMSO) using TMS as an internal standard (chemical shift in d-scale).

2.3.2. Color.

Gardner Colorimeter was used to measure the color, and the results were expressed as Gardner units (GU).

2.3.3. Acid number.

ASTM D974-92 method is used to determine the Acid Number of the prepared surfactants, and the results were expressed in mg (KOH equivalent).g (sample)-1

2.3.4. Hydroxyl number.

ASTM E326-85 method is used to determine the Hydroxyl Number of the prepared surfactants, and the results were expressed in mg (KOH equivalent).g (sample)-1

2.3.5. Saponification number.

Saponification Number was measured to determine the Hydroxyl Number of the prepared surfactants, and the results were expressed in mg (KOH equivalent).g (sample)-1

2.3.6. Surface tension measurements and determination of CMC.

The surface tension measurements were undertaken for different concentrations of the prepared new Ethoxylated carbohydrate-based surfactants dissolved in double distilled water with a surface tension equal 72 mN m\(^{-1}\) at 25 °C according to the method described in ASTM Designation: D1331-89 with a Krüss Tensiometer using a Du Nouy ring at constant temperature (25 ± 1 °C). Apparent surface tension values were given as a mean of three consecutive measurements.

The critical micelle concentrations (CMC) value of the prepared new Ethoxylated carbohydrate-based surfactants were determined using surface tension measurements where surface tension values of aqueous solutions of our prepared surfactants were plotted against the corresponding concentrations. The interrupt change in the surface tension-concentrations curves will express the critical micelle concentration.

2.4. Corrosion inhibition investigation measurements.

2.4.1. Chemical measurements (WL).

Six parallel coins of LCS sheets 2 × 2 × 0.2 cm were prepared by emery paper (grade 320–600–800-1200), washed by distilled water and acetone. After accurate weighing, the specimens were dipped in a 150 ml beaker, which contained 100 ml of HCl with and without the addition of different concentrations of SMS-20-EO, SMO, and SMO-20-EO. All aggressive acid solutions were open to the air. During 3 hours, the specimens were taken out, washed, dried, and weighed accurately by Four-Digit Analytical Balance. The average (WL) of the six parallel coins LCS sheets could be obtained. The % IE and the degree of surface coverage \(\theta\), of non-ionic surfactant for the corrosion of LCS in 1 M HCl were calculated from eq. (1) [30]:

\[
\text{IE \%} = \theta \times 100 = [1 - (W / W^0)] \times 100
\]
Where $W^\circ$ and $W$ are the values of the average WLs without and with the addition of the surfactant, respectively

2.4.2. Electrochemical measurements.

The electrochemical instruments are Gamry Instrument Potentiostat/Galvanostat/ZRA (PCI4-G750) were performed by three electrodes working electrode is LCS, Pt electrodes as an auxiliary electrode, and calomel as a reference electrode (SCE). For the Tafel polarization technique, the potential of $\pm 1.1$ V was applied with a scan rate of 0.5 mVs$^{-1}$. EIS study was carried out with the frequency range between 100 to 0.2 Hz using a 5 mV amplitude. EFM experiments were performed by applying a potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz [31].

2.4.3. Surface examinations.

The coins of LCS used for surface examination were immersed in 1 M HCl in the absence and the presence of 125 ppm of new ethoxylated surfactant at 25°C for 24 hrs. The analysis was performed using a Scanning Electron Microscope (JEOL JSM-5500, Japan).

3. Results and Discussion


3.1.1. Spectroscopic investigation of the newly prepared ethoxylated carbohydrate-based surfactants.

A: FTIR Spectra of the new prepared Ethoxylated carbohydrate-based surfactants:

Figure 1 a, b, c shows FTIR spectrograms of SMO, SMO-20-EO, and SMS-20-EO surfactants, respectively. The structural moieties for the newly prepared ethoxylated carbohydrate-based surfactants that can be justified spectroscopically by infrared spectroscopy are summarized as following [32]. At 3000 cm$^{-1}$ (O–H) associated stretching vibrations, 2900 – 3000 cm$^{-1}$ (sp3C–H) stretching vibrations, 1700 cm$^{-1}$ (C=O) Carbonyl groups, 1400 cm$^{-1}$ (CH2) aliphatic sp3 stretching vibrations and 1100 cm$^{-1}$ (C-O) ether and alcohols Bending vibrations.

![Figure 1](image-url)
Figure 1. (b) FTIR spectrograms of SMO-20-EO (A2).

Figure 1. (c) FTIR spectrograms of SMS-20-EO (A3).

B: $^1$H NMR Spectra of the new prepared Ethoxylated carbohydrate-based surfactants: Figure 2a, b, c represents $^1$H NMR spectrograms of SMS-20-EO, SMO, SMO-20-EO surfactants, respectively. (SMO) compound: $^1$H-NMR (400 MHz) (DMSO d6) $\delta$ 0.6013–0.6320 (t, CH$_3$), 1.0026 (s, CH$_2$), 1.2362–1.2707 (t, CH$_2$), 1.7379–1.7512 (m, CH), 1.9070–1.9434 (t, 2CH), 2.0471 (s, CH$_2$), 2.2714 (s, CH$_2$), 3.1132–3.1747 broad overlap (m, CH$_2$), 5.0877 (s, OH). (SMO-20-EO) compound: $^1$H-NMR (400 MHz) (DMSO d6) $\delta$ 0.8450–0.8614 (t, CH$_3$), 1.2429 (s, CH$_2$), 1.4999 (t, CH$_2$), 1.9793–2.0241 (m, CH), 2.1751–2.2106 (t, 2CH), 2.2922–2.3087 (t, 3CH), 3.4033–3.5940 broad overlap (m, CH$_2$), 5.3181 (s, OH), 8.1448 (s, OH).

(SMS-20-EO) compound: $^1$H-NMR (400 MHz) (DMSO d6) $\delta$ 0.8604 (s, CH$_3$), 1.2401 (s, CH$_2$), 1.5133 (t, CH$_2$), 2.2891 (m, CH), 3.4037–3.5923 broad overlap (m, CH$_2$), 8.1450 (s, OH). Both FTIR and $^1$H NMR results can provide evidence of the synthesis of the novel non-ionic surfactants is successful.
Figure 2. (a) $^1$H NMR spectra of SMO surfactant in DMSO.

Figure 2. (b) $^1$H NMR spectra of SMO-20-EO surfactant in DMSO.

Figure 2. (c) $^1$H NMR spectra of SMS-20-E surfactant in DMSO.
3.1.2. Physical and chemical characterization of the newly prepared ethoxylated carbohydrate-based surfactants.

All properties are summarized in Table 2:

Table 2. Physical and chemical characterization of the newly prepared Ethoxylated carbohydrate-based surfactants.

<table>
<thead>
<tr>
<th>Surfactant / Test Method</th>
<th>SMO</th>
<th>SMS</th>
<th>SMO-20-EO</th>
<th>SMS-20-EO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>7</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Acid Number</td>
<td>3.3</td>
<td>9</td>
<td>2</td>
<td>2.2</td>
</tr>
<tr>
<td>Hydroxyl Number</td>
<td>199</td>
<td>235</td>
<td>74</td>
<td>87</td>
</tr>
<tr>
<td>Saponification Number</td>
<td>154</td>
<td>151</td>
<td>53</td>
<td>49</td>
</tr>
</tbody>
</table>

3.1.3. Surface tension measurements and determination of CMC.

The surface tension (c) of water originates from hydrogen bonds between the water molecules at the air-water interface. If the surfactant adsorbs at the interface, it breaks the hydrogen bonds, and consequently, the surface tension of the water surface will decrease lower than 71.8 mN m\(^{-1}\) at 25 °C. Here, the surface tension of surfactants was measured for different concentrations of the newly prepared Ethoxylated carbohydrate-based surfactants above and below the critical micelle concentration (CMC).

Figure 3 a, b, c represents plots of surface tension versus concentration for the new prepared Ethoxylated carbohydrate-based surfactants in deionized water. The surface tension curve shows an obvious descending as the concentration of aqueous surfactant solution increases.

This means that the surfactant molecules are highly adsorbed at the water interface. As long as the concentration of the surfactant molecules increases, the surface tension values will remain stable. When these two regions are intercepted, this gives the concentration at which the surfactant micelles are formed (CMC). This observation was recorded for the newly prepared Ethoxylated carbohydrate-based surfactants up to the CMC, beyond which no considerable changes were noticed. The CMC data obtained from the intercept in the concentration plots is shown in Table 3. The ethylene oxide EO molecules increase the hydrophilicity of the non-ionic surfactants due to the ether bond leads to increasing CMC values and increasing in the depression of the surface tension at this concentration.

Table 3. Surface tension (γ) and critical micelle concentration (C_{cmc}) of the newly prepared Ethoxylated carbohydrate-based surfactants from surface tension measurements at 25 °C.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>γ Surface tension (mN(\cdot)m(^{-1}))</th>
<th>CMC, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMO</td>
<td>28.7</td>
<td>125</td>
</tr>
<tr>
<td>SMO-20-EO</td>
<td>34.5</td>
<td>250</td>
</tr>
<tr>
<td>SMS-20-EO</td>
<td>37.2</td>
<td>700</td>
</tr>
</tbody>
</table>

Figure 3. (a) Surface tension of SMO surfactant versus its concentrations in water at 25 °C.
Figure 3. (b) Surface tension of SMO-20-EO surfactant versus its concentrations in water at 25 °C.

Figure 3. (c) Surface tension of SMS-20-EO surfactant versus its concentrations in water at 25 °C.

3.2. WL measurements.

WL of LCS was determined, at various time intervals, in the absence and presence of a different concentration of surfactants (SMS-20-EO, SMO, and SMO-20-EO). The increase in the surfactant concentration was accompanied by a decrease in WL and an increase in the %IE. These results lead to the conclusion that new surfactants under investigation are fairly efficient inhibitors for LCS dissolution in HCl solution. Also, the surface coverage (Θ) while \( \theta = \frac{\text{IE} \%}{100} \) by the surfactants, would increase with increasing the surfactant conc. Corrosion Rate (C.R.) in mg cm\(^{-2}\) min\(^{-1}\) is decreased with the increase of the surfactant concentration. These results are summarized in Table 4.

3.2.1. Effect of temperature.

The effect of temperature on the corrosion rate of LCS in 1 M HCl and with the absent and presence of different surfactant conc. was studied in the temperature range of 25 –45 °C uses WL measurements. As corrosion rate (C.R.) increases, the temperature is increased, and the IE% of the surfactants decreases as shown in Table 4. The adsorption behavior of surfactants on the LCS surface occurs through physical adsorption.

Table 4. Values of IE% and (C.R.) of surfactants (SMO&SMO-20-EO&SMS-20-EO) for the corrosion of LCS in 1 M HCl from WL measurements at different concentrations and a temperature range of 25 –45 °C.

<table>
<thead>
<tr>
<th>[Inh.] ppm</th>
<th>298K</th>
<th>303K</th>
<th>308K</th>
<th>313K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMO</td>
<td>C.R</td>
<td>%IE</td>
<td>C.R</td>
<td>%IE</td>
<td>C.R</td>
</tr>
<tr>
<td>25</td>
<td>0.0120</td>
<td>66</td>
<td>0.0135</td>
<td>77</td>
<td>0.0268</td>
</tr>
</tbody>
</table>
From the previous result, we can express adsorption quantitatively by deriving the adsorption isotherm that characterizes the metal/surfactant/environment system. Various adsorption isotherms were applied to fit θ values, SMS-20-EO, SMO, and SMO-20-EO, respectively.

### 3.2.2. Adsorption isotherms.

Langmuir adsorption isotherm is the best-fit isotherm because its regression constant is nearly unity and expressed by [33]:

\[
C \theta = 1K_{ads} + C
\]  

Where C is the concentration (ppm) of the new surfactants in bulk electrolytes, \( K_{ads} \) are adsorption equilibrium constant. A plot of \( C\theta \) versus C (Fig.4) at different temperatures.
should give straight lines with a slope approximately equals unity, and the \( K_{\text{ads}} \) equal \( \frac{1}{55.5} \) intercept. In order to get a comparative view, the variation of the \( (K_{\text{ads}}) \) of the surfactants with their concentrations was calculated according to Eq. (2). The experimental data give good curves fitting for the applied adsorption isotherm as the correlation coefficients \( (R^2) \) were in the range (0.97-0.98). The values obtained are given in Table 5. The \( K_{\text{ads}} \) is related to the free energy of adsorption \( \Delta G^{\circ}_{\text{ads}} \) as follows [34]:

\[
K_{\text{ads}} = \frac{1}{55.5} \exp \left[-\Delta G^{\circ}_{\text{ads}} / RT \right] \tag{4}
\]

Where 55.5 is the molar concentration of water in the solution in M \(^{-1}\), \( R \) is the gas constant, and \( T \) is the absolute temperature.

Plots of \((\log K_{\text{ads}}) \) vs. \( (1000 / T) \) Figure 5 gave the heat of adsorption \( \Delta H^{\circ}_{\text{ads}} \) and the standard entropy \( \Delta S^{\circ}_{\text{ads}} \) according to the basic thermodynamic eq. (5)

\[
\Delta G^{\circ}_{\text{ads}} = \Delta H^{\circ}_{\text{ads}} - T \Delta S^{\circ}_{\text{ads}} \tag{5}
\]

Table 5 clearly showed a good dependence of \( K_{\text{ads}} \) on \( T \), indicating the good correlation among thermodynamic parameters. The negative value of \( \Delta G^{\circ}_{\text{ads}} \) refers to the spontaneity of the adsorption process and stability of the adsorbed layer on the LCS surface. Generally, values of \( \Delta G^{\circ}_{\text{ads}} \) around \(-20 \) kJ mol\(^{-1}\) or lower are consistent with the physical adsorptions as electrostatic interaction between the charged atom on surfactants and the charged metal. While around \(-40 \) kJ mol\(^{-1}\) or higher involve charge transfer from surfactants to the metals to form a coordinate bond (chemisorption) [35]. The values of \( \Delta G^{\circ}_{\text{ads}} \) obtained were approximately equal to \(-25 \pm 1 \) kJ mol\(^{-1}\), which means that the adsorption mechanism of the new surfactants on LCS in 1 M HCl involves both electrostatic adsorption and physical adsorptions [36]. The thermodynamic parameters point toward both physical adsorption as major contributors and chemisorption as minor contributors of the new surfactants onto the surface of the metal. The \( K_{\text{ads}} \) follows the same behavior in that large values of \( K_{\text{ads}} \) suggest good, more efficient adsorption and hence good inhibition efficiency. The values of the thermodynamic parameter for the adsorption of surfactants Table 5 can provide valuable information’s about the mechanism of corrosion inhibition.

<table>
<thead>
<tr>
<th>Inh.</th>
<th>Temp. °C</th>
<th>( K_{\text{ads}} ) M(^{-1})x10(^{-3})</th>
<th>( -\Delta G^{\circ}_{\text{ads}} ) kJ mol(^{-1})</th>
<th>( -\Delta H^{\circ}_{\text{ads}} ) kJ mol(^{-1})</th>
<th>( -\Delta S^{\circ}_{\text{ads}} ) J mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMO-20-EO</td>
<td>25</td>
<td>26.73082</td>
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</table>

While an endothermic adsorption process \((\Delta H^{\circ}_{\text{ads}} > 0)\) is attributed unequivocally to chemisorption [37], an exothermic adsorption process \((\Delta H^{\circ}_{\text{ads}} < 0)\) may involve either physical adsorption or chemical adsorption or a mixture of both processes. In the presented case, the calculated values of \( \Delta H^{\circ}_{\text{ads}} \) for the adsorption of surfactants in 1 M HCl, indicating that this

https://doi.org/10.33263/BRIAC112.93829404
surfactant may be physical adsorbed. The \( \Delta S_{ads} \) values in the presence of surfactants in 1 M HCl are negative. This indicates that an increase in disorder takes place on going from reactants to the metal-adsorbed reaction complex [38].

3.2. Electrochemical measurements.

3.2.1. Polarization (PP) measurement.

Figure 6 shows the polarization behavior of LCS in 1 M HCl electrolyte. In the absence and presence of various concentrations of surfactants, we can see clearly that both the anodic and cathodic branches of the polarization curve exhibit a typical Tafel behavior. The corrosion rate can be determined by the Tafel extrapolation method [39]. Table 6 shows the electrochemical parameters (\( i_{corr} \), \( E_{corr} \), \( \beta_a \), \( \beta_c \), and IE %) associated with polarization measurements of LCS in 1 M HCl electrolytes in the absence and presence of different concentrations of surfactants.

A probe of Table 6 shows that the corrosion current (\( i_{corr} \)) decreased, and %IE increased with increased surfactant concentration. Also, \( \beta_a \), \( \beta_c \) values changed slightly with the addition of the surfactants, indicating that this surfactant functions through blocking the reaction sites on the metal surface without changing the anodic and cathodic reaction’s mechanism. If the largest displacement of \( E_{corr} \) value surpasses ± 85 mV, the inhibitor can be cathodic or anodic type inhibitor [40]. According to the \( E_{corr} \) values listed in Table 6, the largest \( E_{corr} \) shift is, which indicates that the surfactants can be classified as a mixed-type inhibitor. The values of IE% were calculated using the following equation:

\[
\%IE = \theta \times 100 = \left[ 1 - \left( \frac{i_{corr}}{i^{*}_{corr}} \right) \right] \times 100
\]  

(8)
Where \( i_{\text{corr}} = \text{corrosion current density without surfactant} \) and \( i_{\text{corr}} = \text{corrosion current density with a surfactant} \), the orders of IE\% of all surfactants at a different concentration as given by polarization measurements are listed in Table 6. The results are in good agreement with those obtained from WL measurements and order as follows: SMO-20-EO > SMS-20-EO > SMO.

### Table 6. \((E_{\text{corr}}, \,(i_{\text{corr}}, \,(\beta_a, \beta_d), \,(\theta), \text{and } \% \text{IE}) \text{ of LCS } 1 \text{ M HCl at } 25^\circ\text{C for surfactants.} \)

<table>
<thead>
<tr>
<th>Comp</th>
<th>Conc., ppm</th>
<th>(i_{\text{corr}}), (\mu\text{A cm}^{-2})</th>
<th>(-E_{\text{corr}}, \text{mV vs SCE})</th>
<th>(\beta_a, \text{mV dec}^{-1})</th>
<th>(\beta_d, \text{mV dec}^{-1})</th>
<th>C.R mpy</th>
<th>(\theta)</th>
<th>% IE</th>
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<td>76.9</td>
<td>179.4</td>
<td>45.61</td>
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<td>0.9268</td>
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3.2.2. Electrochemical impedance spectroscopy (EIS) measurements.

The impedance analysis gives us information about the properties of a surface, mechanism of actions, and kinetics of electrodes with surfactant in electrolytes as corrosive media [41]. Figure 7 contains a- Nyquist plots at open-circuit potential, all in the absence and presence of the new surfactants at 25°C. By increasing the concentration of each surfactant lead to increase double capacitance layers and decreases C\(_{dl}\) Values with respect to the blank (without inhibitors). Figure 7a enhances that. So, at certain surfactants concentration, the inhibitions efficiency following the orders: SMO-20-EO > SMS-20-EO > SMO. From the theory of EIS, the Nyquist plots don’t yield perfect semicircles as expected. The deviation from the ideal semicircle was generally attributed to the frequency dispersion [42] as well as to the inhomogeneity of the surface. Surfactants inhibit corrosion primary through its adsorption on the metal surface. The point of intersection between the depressed semicircle and real axis represents (Rs + Rct) [43]. To obtain C\(_{dl}\), the frequency (f\(_{\text{max}}\)) at which the imaginary component of the impedance is maximal was found. The %IE of the inhibitor was evaluated by R\(_{ct}\), C\(_{dl}\) and the maximum phase angle (\(\theta_{\text{max}}\)) should be 90° for corrosion interface represented by a simple R-C parallel equivalent circuit when Rs=0. However, depressed semicircles are usually obtained for practical electrode/solution interface, which has been known to be associated with the roughness of the electrode surface. Corrosion of LCS in 1 M HCl solutions increases the roughness of the electrode surface and therefore reduces the values of \(\theta_{\text{max}}\). A less depressing semicircle (with a higher maximum phase angle close to 90°) also indicates better quality of inhibitor monolayer.

EIS spectra of the investigated surfactants were analyzed using the equivalent circuit, Figure 8, which represents a single charge transfer reaction and fits well with our experimental
results. The constant phase element, CPE, is introduced in the circuit instead of a pure double-layer capacitor to give a more accurate fit [44]. The double-layer capacitance, \( C_{dl} \), for a circuit including a CPE parameter (\( Y_0 \) and \( n \)) were calculated from eq.9 [45]:

\[
C_{dl} = Y_0 (\omega_{max})^{-n-1}
\]  

(9)

where \( Y_0 \) is the magnitude of the CPE, \( \omega_{max} = 2\pi f_{max} \), \( f_{max} \) is the frequency at which the imaginary component of the impedance is maximal, and the factor \( n \) is an adjustable parameter that usually lies between 0.5 and 1.0. After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircle, showing that the corrosion process was mainly charged-transfer controlled [46]. The general shape of the curves is very similar for all samples (in the presence or absence of surfactants at different immersion times), indicating that no change in the corrosion mechanism [47]. From the impedance data Table 7, we concluded that the value of \( R_{ct} \) increases with increasing the concentration of the surfactants, and this indicates an increase in % IE\textsubscript{EIS}. Which in concord with the WL and PP results obtained. In fact, the presence of surfactants enhances the value of \( R_{ct} \) in acidic solution. Values of double-layer capacitance are also brought down to the maximum extent in the presence of surfactant, and the decrease in the values of CPE follows the order like that obtained for \( i_{corr} \) in this study. The decrease in CPE/\( C_{dl} \) results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggesting that organic derivatives inhibit the LCS corrosion by adsorption of metal/acid [48]. The %IE was calculated from the charge transfer resistance data from eq.10 [49]:

\[
\% \text{IE}_{\text{EIS}} = [1 - (R_{ct}^o / R_{ct})] \times 100
\]  

(10)

Where \( R_{ct}^o \) and \( R_{ct} \) are the charge-transfer resistance values with and without surfactant, respectively.

Figure 7. The Nyquist plots for the corrosion of LCS in 1 M HCl in the absence and presence of different Conc. of surfactants at 25\(^\circ\)C.

Figure 8. Equivalent circuit model used to fit experimental EIS.
Table 7. Electrochemical kinetic parameters were obtained by the EIS technique for in 1 M HCl without and with various concentrations of surfactants at 25°C.

<table>
<thead>
<tr>
<th>Comp</th>
<th>Conc., ppm</th>
<th>Rct, Ω cm²</th>
<th>Cdl, x 10⁻⁴ Fcm⁻²</th>
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<th>%IE</th>
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3.2.2. Electrochemical frequency modulation (EFM) measurements.

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current values without prior knowledge of Tafel slopes and with only a small polarizing signal. These advantages of the EFM technique make it an ideal candidate for online corrosion monitoring [50]. The great strength of the EFM is the causality factors, which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Figure 9 shows the EFM intermodulation spectra (current vs. frequency) of LCS in HCl solution containing different concentrations of surfactants. The larger peaks were used to calculate the corrosion current density (i corr), the Tafel slopes (βa and βc), and the causality factors (CF-2 and CF-3). These electrochemical parameters were listed in Table 8.

Table 8. Electrochemical kinetic parameters were obtained from the EFM technique for LCS in 1 M HCl in the absence and presence of different concentrations of surfactants.

<table>
<thead>
<tr>
<th>Comp</th>
<th>Conc., ppm</th>
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<th>βa, mVdec⁻¹</th>
<th>βc, mVdec⁻¹</th>
<th>C.R., mpy</th>
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Figure 9. EFM spectra of LCS in 1 M HCl in the absence and presence of different Conc. of surfactants at 25°C.

The data presented in Table 8, obviously showed that the addition of any one of the tested compounds at a given concentration to the acidic solution decreases the corrosion current
density, indicating that these surfactants inhibit the corrosion of LCS in 1 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3), indicating that the measured data are verified and of good quality. The % IE_{EFM} increases by increasing the surfactant concentrations and was calculated as in Eq. (8). The IE obtained from this method is in the order: SMO-20-EO > SMS-20-EO > SMO.

3.3. Surface examinations.

3.3.1. Scanning electron microscopy (SEM) analysis.

As shown in Fig.10a SEM for the LCS surface shows the LCS surface image in the air without an explosion in any media. Fig. 10b-e Shows surface destroy of the LCS after immersion in the corrosive media in the absence and presence of the surfactant for 24 hrs. In the absence of the surfactant, the results exhibited that a thick porous layer of corrosion product (oxide film) covers the entire metal surface; the surface was strongly damaged, so the surface of the metal cannot be seen. While Fig. 10c-e presents the image of the electrode surface in the presence of 125 ppm of surfactants (SMO-20-EO > SMS-20-EO > SMO). The images of Fig.10c,e showed that the surface is almost free from damages, and it is smooth, this indicates the presence of a good protective film present on the LCS surface, also confirms the highest IE% of the investigated new ethoxylated surfactants.

3.4. Mechanism of surfactant inhibition.

In the present work, the mechanism of corrosion inhibitions have a complex process that begins with the formation of a monolayer as a protective layer on the surface of the metal. This protective layer depends on many factors such as the concentration of surfactant inhibitor, temperature, and nature of the corresponding surface, the interaction between surfactant inhibitor and substrate, and chemical reactions. The adsorption of a surfactant molecule on the surface of a metal in the corrosive media is the first state on the mechanism actions. This protective process is influenced by the surface charge of the metal, the chemical composition of surfactant inhibitors, and types of corrosive electrolytes. The following equation illustrates the adsorption reaction occurs on the metal surface by surfactant molecules.

\[
\text{Surfactant}_{\text{Sol.}} + n\text{H}_2\text{O}_{\text{ads}} = \text{Surfactant}_{\text{ads.}} + n\text{H}_2\text{O}_{\text{Sol.}}
\]

While n is the number of water molecules replaced by the surfactant molecules adsorbed on the metal surface, it’s clear that the amount of (n) is related to the surfactant inhibitor size respected with the water molecules. The keyword of surfactant inhibition was its functions group adsorbed on the metal surface. So, the corrosion inhibition is related to the adsorption ability of the surfactant molecule on the surface of the metal, which is directly related to the capacity of a surfactant molecule to aggregate to form micelles. The critical micelle concentration CMC is the main factor in determining the effectiveness of the corrosion inhibitor. Under CMC, by increasing the surfactant concentration, the molecules tend to aggregate at the interface, and this interfacial aggregation reducing the surface tension. Above CMC, the metal surface was completely covered with a monolayer by surfactant molecules. The corrosion rate (C.R.) increases with increasing the immersion time. This leads to the dissolution of the iron as the component of the main item of LCS to form an oxide film as a corrosion product, which reduces the corrosion by the time [51]. The influence on increase
temperature of electrolytes leads to increase corrosion rate due to the desorption of surfactant molecules from metals surface.

![Scanning Electron Microscope graphs of LCS surface.](image1)

**Figure 10.** (a-e) Scanning Electron Microscope graphs of LCS surface. a) Before immersion in 1 M HCl, b) after 24 hrs. Of immersion in 1 M HCl and c) after 24 hrs. Of immersion in 1 M HCl + 125 ppm of surfactant (SMO-20-EO) and d) after 24 hrs. Of immersion in 1 M HCl + 125 ppm of surfactant (SMS-20-EO), e) after 24 hrs. Of immersion in 1 M HCl + 125 ppm of surfactant (SMO) at 25°C.

### 4. Conclusions

The new ethoxylated surfactant has good applications as green corrosion inhibitors. IE % inhibitions the efficiency of the new ethoxylated surfactant increase by increasing its concentration. Until reaching Maximum value at (CMC). The IE% depends on the temperature, the concentration of new surfactant inhibitors, and its chemical structure, which appear obviously in the following order according to IE% is: SMO-20-EO > SMS-20-EO > SMO. While The IE % increases as the length of the hydrocarbon chain are increased, and the unsaturated double bond increase. The current new ethoxylated surfactant is mixed type corrosion inhibitors in HCl electrolytes due to its inhibition action on both the anodic process of metal dissolution and the cathodic process of hydrogen evolution. By adding the surfactant leads to a decrease in the double layer capacitance with respect to the blank due to the formation of barriers films by adsorptions phenomenon, which leads to raising IE%. The adsorption of new non-ionic surfactants on LCS in HCl electrolytes obey Langmuir adsorption isotherm. The percentage of IE% of surfactants obtained from the Weight loss, Polarization, E-Impedance, and E-Frequency Modulation techniques are in good agreement.
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Conflicts of Interest

The authors declare that they have no conflict of interest.

References


