Use of an imidazol synthetized from palm oil as a corrosion inhibitor for a supermartensitic stainless steel in H$_2$S

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ABSTRACT
A no-ionic gemini surfactant, namely bis(2-((2-palmitoamidoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate, was synthesized from the fatty acids contained in the palm oil and evaluated as corrosion inhibitor for UNS S41425 type supermartensitic stainless steel in presence of H$_2$S. Used techniques involved potentiodynamic polarization curves, linear polarization resistance and electrochemical impedance measurements. Additionally, the obtained inhibitor was characterized by Infrared and 1H, 13C RMN spectroscopy. Results have shown that the corrosion rate of the steel was markedly decreased by the addition of the imidazole-type of inhibitor, reaching its maximum efficiency at certain inhibitor concentration, decreasing with a further increase in its concentration. This decrease in the corrosion rate was due to the physical adsorption of the inhibitor on to the steel surface following a Langmuir type of adsorption isotherm, affecting both anodic and cathodic reactions.

1. Introduction
The constant increase in oil and gas demand has made reserves, previously not considered economically feasible, to become viable sources of energy. However, such reserves demand specific project solutions, considering their unique features. One family of materials that is being used as a solution to moderate H$_2$S and CO$_2$ effects is the super martensitic stainless steel, which can contain 13 to 16%Cr and up to 5%Mo for improved corrosion resistance (7). However, despite of their high corrosion resistance in these environments, some failures of this type of stainless steels have been found in service (2, 3). In most cases, failures are related to hydrogen embrittlement induced by the presence of hydrogen sulphide (H$_2$S), uniform and pitting corrosion (1, 3, 4), but the associated corrosion mechanisms are not completely unveiled (5–8). One of the most commonly used practices to fight corrosion is the use of organic inhibitors because they can effectively retard the corrosion of steel through forming a compact barrier film between steel surface and corrosive medium (9–12). Most organic corrosion inhibitors contain heteroatoms, such...
as nitrogen, oxygen, phosphorus and sulphur as well as triple bond or aromatic ring, considered as the reaction center for the adsorption process (13–15) because the heteroatoms can donate their lone electron pairs to the empty d-orbitals of Fe atoms to form the coordinate covalent bonds (16, 17). Some of the most frequently used organic inhibitors include amines (10, 11), amides (15), imidazole and imidazolines (16, 17). Moreover, in some cases, the electrostatic interaction between inhibitor molecules and steel surface is also favorable for the adsorption of inhibitors (18–20). However, due to serious environmental concerns, in the last few years there has been a big interest for the called “green inhibitors” which includes extracts from plants which also contain heteroatoms and are non toxic, environmentally friendly, non-hazardous, cheaper and readily available. Many of these naturally-occurring inhibitors have been extracted from essential oils contained in plants (21–31). Thus, Asmaa and El-Dougdoug (21) extracted an amido poly amine surfactant from the Melia azedarach seeds oil and used it as a corrosion inhibitor for carbon steel in 2.0M HCl by using potentiodynamic polarization curves and electrochemical impedance spectroscopy. They found that the surfactant acts as a mixed type of inhibitor and it is physically adsorbed on to carbon steel by following a Langmuir type of adsorption. Similarly, Porcayo-Calderon et al. (31) synthetized an imidazoline from the essential oil contained in the coffee bagasse and used it as a corrosion inhibitor for carbon steel in a CO2-saturated 3.5% NaCl solution + diesel emulsion at 50°C by using electrochemical techniques, finding an optimal doses of 10 ppm. Finally, Salinas-Solano et al. (30) obtained an amide from rice bran oil and used it as corrosion inhibitor for 1018 carbon steel in CO2-saturated 3.5% NaCl, finding that 25 ppm of this inhibitor was the optimum concentration to obtain efficiency values as high as 99%. Thus, the goal of this research paper is to evaluate the bis(2-(2-palmitoamidoetil) amino) etil 1H-imidazol-4,5-dicarboxilate obtained from palm-oil as a corrosion inhibitor of a supermartensitic stainless steel in an H2S-containing environment.

2. Experimental procedure

2.1. Testing material

Materials used in this research work includes UNS S41425 type supermartensitic stainless steel with a chemical composition as given in Table 1. Cylindrical coupons having 6.0 mm in diameter and 10.0 mm in length were prepared and encapsulated in commercial polymeric resin. Specimens were abraded down to 600 grade emerging paper and rinsed with acetone.

2.2. Testing solution.

Traditionally, when simulating H2S containing solutions for lab testing, brine solutions saturated with H2S gas according to the NACE Standard TM 177 are normally used (32). However, due to problems rising with the toxicity, flammability and corrosiveness of H2S gas, several authors have suggested as alternative sour gas simulating solution the use of 5.0 wt. % NaCl + 2.5% Acetic acid + 10−6 M sodium thiosulphate (Na2S2O3) solution in distilled water (33–37). A completely sealed glass cell was used for the experiments. Before starting, solution was continuously deaerated with nitrogen gas during 60 min. After this, inhibitor was added and the open circuit potential value (OCP) was monitored during 60 min.

2.3. Synthesis and characterization of the inhibitor.

4, 5-Imidazoledicarboxylic acid and N-(2-hydroxyethyl) aminoethylamine were purchased from Sigma Aldrich. The palm oil used were industrial-grade Olefins. The toluene solvent was acquired from Meyer. The synthesis of Gemini surfactants from palm oil was performed in two steps as showed in Figure 1. First, the palm oil was transformed in fatty amide through the aminolysis direct of oil, as we reported previously (38). The mixture of fatty amides was washed with brine and the fatty solid was dried in vacuum. In the second step, the fatty amide (2 mol) was condensed with 4, 5-Imidazoledicarboxylic acid (1 mol), in toluene (seven parts) at reflux. The system was equipped with a Dean Stark apparatus, in order to removal the water and complete the reaction. The progress of reaction was confirmed using thin layer chromatography TLC. The TLC conditions were using silica as support, methanol – methylene chloride (2:8) solution as eluent, and a bromocresol green solution as a developer. The complete di-ester condensation was observed after 6 h of reaction. The solvent was removed and the product was obtained as a slightly yellow paste. The crude of the reaction was characterized by IR and RMN (1H and 13C) spectroscopy. To know fatty

| C   | Mn | Si | Cr | Ni | Mo | S  | P   | Cu  | N  | Fe   |
|-----|----|----|----|----|----|----|-----|-----|----|-----|
| 0.02| 0.75| 0.3| 13.5| 4.7| 1.7| 0.0003| 0.016| 0.07| 0.07| Bal. |
acid profile contained in palm oil, the triglyceride was trans-esterified. Fatty acid methyl esters were analyzed by gas chromatography (GC) with a flame ionization detector (FID). Peaks of fatty acid methyl esters were identified by matching their relative times with those of commercial standards (FAME). Palm oil, Fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide and bis(2-((2-palmitoamidoetil) amino) ethyl) 1H-imidazol-4,5-dicarboxilato were characterized by Infrared spectroscopy in a Bruker Tensor 27 FT-IR Spectrophotometer (Pike Miracle Single-Bounce ATR Cell). Molecular characterization of Gemini Surfactants by H1 y C13 NMR, was performed in a Bruker Avance III de 300 MHz equipment. Inhibitor concentrations were 0, 5, 10, 25, 50 and 100 ppm.

2.4. Electrochemical techniques.

Employed electrochemical techniques included potentiodynamic polarization curves, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) measurements. In all cases, a saturated calomel electrode and a graphite rod were used as reference and auxiliary electrodes respectively. For the potentiodynamic polarization curves, specimens were polarized from $-600$ to $+600$ mV with respect to the open circuit potential value (OCP) at a scan rate of 1 mV/s. For measuring the pitting potential value, $E_{\text{pit}}$ cyclic polarization curves were performed in a similar way to the potentiodynamic polarization curves, but once the passive region was found, polarization continued until the anodic current density increased three orders of magnitude, and then polarization was reversed. Corrosion current density values, $i_{\text{corr}}$, were calculated by using Tafel extrapolation. For the LPR measurements, specimens were polarized ± 15 mV with respect to the $E_{\text{corr}}$ value at a scan rate of 1 mV/s every 60 min during 24 h. Finally, EIS measurements were performed at the $E_{\text{corr}}$ value by applying a signal ± 15 mV peak to peak in the frequency interval of 0.05 to 30,000 Hz. All the experiments were carried out at a temperature of 60°C under static conditions. Surface of corroded specimens were analysed in a Scanning electronic microscope (SEM) whereas micro chemical analysis was performed with an energy dispersive X-ray analyser (EDX) attached to it.

3. Results and discussion

3.1. Inhibitor characterization

Oleic acid is the major fatty acid contained in the palm oil with 44.9%, followed by 35.11% of palmitic acid. In Table 1 the profile of fatty acids contained in the palm oil is shown, it is accord to reported (39). The triglyceride characterization by IR spectroscopy of palm oil, Figure 2, shows a very strong signal at 1743 cm$^{-1}$ for the C = O stretching ester vibration. This signal is shifted to lower frequency at 1642 cm$^{-1}$ for the fatty amides (33). For gemini surfactant, this signal is shown at 1720 cm$^{-1}$ corresponding to the ester group. The imidazole heterocycle presents two bands due to C = C and C = N stretch in the ring at 1560 and 1470 cm$^{-1}$. At 1080 cm$^{-1}$ the signal for C – H stretch of the ring appears. The N-H imidazole presents a broad band at 3150 cm$^{-1}$ due to aromaticity of the ring and other signal which has been assigned to the N-H amide stretch. The C = O stretch of the amide is shifted to 1630 cm$^{-1}$. For stretching of C – N and C – O there
are two bands at 1280 and 1200 cm\(^{-1}\) respectively. Finally, the methyl and methylene groups appears at 2920 and 2852 cm\(^{-1}\).

In the NMR spectrum, Figure 3, it is mainly observed the mixture bis{(2-oleamidoethyl)amino}ethyl 1H-imidazole-4,5-dicarboxylate (45.7%) and bis{(2-palmitamidoethyl)amino}ethyl 1H-imidazole-4,5-dicarboxylate (35%). Symmetrical chemical shift 1H NMR (300 MHz, CDCl\(_3\) \(\delta =7.3\)) for gemini surfactant, \(\delta = 0.87\) (td, 11H, 29), 1.236 (m, 79H, 15–18 and 23–28 (40) for oleic gemini and 15 for palmitic gemini), 1.595 (m, 7H, 14), 1.989 (t, 7 H, 13), 2.139 and 2.342 (2t, 4H, 19), 2.632 and 2.735 (t and q, 4H, 22), 3.096 (td, 4 H, 7), 3.206 (s, N-H), 3.488 (m, 8H, 15–18 and 23–28) for oleic gemini and 15 for palmitic gemini, 1.595 (m, 7H, 14), 1.989 (t, 7 H, 13), 2.139 and 2.342 (2t, 4H, 19), 2.632 and 2.735 (t and q, 4H, 22), 3.096 (td, 4 H, 7), 3.206 (s, N-H), 3.488 (m, 8H, 7and 9), 3.792 and 3.944 (m, 12H, 6 and 10), 5.32 (td, 4 H20, 21), 7.44 and 7.49 (2s, CONH), 7.8 (s, 2 H2). 13C RMN (400 MHz, CDCl\(_3\) \(\delta =77\)) for gemini surfactant: \(\delta = 14.06\) (C29), 22.63 (C28), 25.64 (C14), 27.5 (C19 and 22), 29.04 - 29.72 (C29), 31.86 (C27), 36.37 and 36.02 (C13), 43.21 and 43.34 (C10), 48.71 and 49.11 (C9), 50.51 and 51.78 (C7), 57.67 and 58.67 (C6), 129.69 and 129.96 (C20 and 21), 132.43 (C4), 137.27 (C2), 165.04 (C5), 170.82 and 174.54 (C12).

### 3.2. Open circuit potential

The effect of the inhibitor concentration on the change in the OCP value with time is shown in Figure 4. In these tests, inhibitor was added after a pre-corroding time of approximately 500 s. In absence of inhibitor, the OCP value began around at \(-490\) mV and it shifted towards slightly more active values as time elapsed, reaching a more or less stable value, close to \(-510\) mV after 1000 s of exposure and remained there during the rest of the test. When 5 ppm of inhibitor were added, the OCP value was shifted towards slightly nobler values, although this shift was marginal, less than 20 mV. However, when doses of inhibitor higher or equal than 10 ppm, the OCP value shifted towards nobler values, moving from an initial value of \(-490\) mV up to a stable value of \(-340\) mV regardless of the inhibitor concentration. The time to reach this steady value became shorter as the inhibitor concentration increased. Normally, the more active the OCP value is, the higher the susceptibility of that metal to be corroded. When iron or steel are an H\(_2\)S-containing solution, a layer of corrosion products consisting mainly of different forms of iron sulfide (FeS) is formed (40–44). Changes in the temperature, partial pressure, etc… can make that iron sulfide film protective or non-protective and have different morphology and crystallographic structure, being the most common mackinawite, troilite, pyrrhotite and cubic FeS (42–44). However, according to chemical composition given in Table 1, the presence of chemical elements such as Cr, Ni and Mo should be expected in this layer. Lei et al. (8) studied the electrochemical behavior of a 13-Cr martensitic stainless steel in a H\(_2\)S-saturated NaCl solution, and found that the corrosion products scale consisted mainly of non-protective Fe, Cr Ni and, probably Mo sulfides. Thus, the shift of the OCP value towards more active values is because the metal is undergoing anodic dissolution and the formation of sulfides is taking place. On the contrary, when the OCP value is shifting towards nobler values, as it occurs with the addition of doses higher than 10 ppm of inhibitor, is because a layer of protective corrosion products is taking place.

### 3.3. Potentiodynamic polarization curves

The effect of inhibitor concentration on the polarization curves for the UNS S41425 type supermartensitic stainless steel in the H\(_2\)S-containing NaCl solution is given.
in Figure 5 whereas a typical cyclic polarization curve is given in Figure 6. It can be seen that in all cases, regardless of the inhibitor concentration, curves display an active–passive behavior as reported before (33, 38, 45).

For the uninhibited solution, the $E_{corr}$ value was the most active one, with a value of $-520 \text{ mV}$ and a corrosion current density value of $8 \times 10^{-4} \text{ mA/cm}^2$, the highest value exhibited by the steel in this solution, as shown in Table 2. As the applied potential is made more anodic, the metal corrodes with the formation of corrosion products until a passive layer is formed. The passivation zone started at a potential value close to $-100 \text{ mV}$ and ended at a pitting potential value, $E_{pitting}$, of $-85 \text{ mV}$. The passivation current density value in this case was $7 \times 10^{-4} \text{ mA/cm}^2$, very similar to a typical passivation current density for this kind of steels in $\text{H}_2\text{S}$-containing environments which is lower than $1 \times 10^{-3} \text{ mA/cm}^2$ (33–35). It has been established that the passive layer is formed of nickel, molybdenum, and in less amount chromium and iron sulfides (33, 38, 45) and it is the responsible for the decrease in the corrosion rate of the steel.

When the inhibitor is added, the $E_{corr}$ value becomes nobler and the corrosion current density value decreases reaching its lowest value, $6 \times 10^{-6} \text{ mA/cm}^2$, see Table 2, when 25 ppm of inhibitor are added, increasing again with a further increase in the inhibitor concentration. Inhibitor efficiency also increased with the inhibitor concentration, reaching its highest value with the addition of 25 ppm, decreasing with a further increase in the inhibitor concentration. In this case, inhibitor efficiency, $I.E.$ was calculated by using:

$$I.E.(\%) = \left( \frac{i_{corr} - i'_{corr}}{i_{corr}} \right) \times 100$$

where $i_{corr}$ is the current density value with no inhibitor and $i'_{corr}$ is the current density value with inhibitor respectively. Additionally, the metal surface area covered by the inhibitor, $\theta$, which is obtained by dividing the inhibitor efficiency value by 100, also increased with increasing the inhibitor concentration, reaching its highest value at an inhibitor concentration of 25 ppm, decreasing with a further increase in the inhibitor concentration, which indicates that the decrease in the $i_{corr}$ value is due to the inhibitor adsorption on top of the metal. This is because the heteroatoms such as N and O can donate their lone electron pairs to the empty d-orbitals of Fe atoms to form the coordinate covalent bonds (11, 12). Moreover, in some cases, the electrostatic interaction between inhibitor molecules and steel surface is also favorable for the adsorption of inhibitors (13–15). When there is a supersaturation of the inhibitor molecules on the metal surface, on the other hand, can cause some electrostatic repulsion among them causing desorption of the inhibitor molecules, with an increase in the corrosion current density value (11–15) as observed for inhibitor concentrations higher than 25 ppm.

The passivation current density value, $i_{pass}$, also decreased with the addition of the inhibitor, reaching

**Table 2. Fatty acid composition of palm oil.**

| Fatty acids | Structure | Type of fatty acid | Palm oil (wt%) |
|------------|-----------|-------------------|---------------|
| Palmitic acid | C16:0 | Saturated | 35.12 |
| Stearic acid | C18:0 | Saturated | 4.32 |
| Oleic acid | C18:1 n-9 cis | Unsaturated | 45.74 |
| Linoleic acid | C18:2 n-6 cis | Unsaturated | 10.23 |
| Linolenic acid | C18:3 n-3 cis | Unsaturated | 0.44 |
| Arachidic acid | C20:0 | Unsaturated | 0.41 |

![Figure 5. Effect of bis(2-((2-palmitoamidoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate concentration on the potentiodynamic polarization curves for UNS S41425 type supermartensitic stainless steel corroded a H2S-containing solution at 50°C.](image)

![Figure 6. Typical cyclic polarization curve for the determination of the pitting potential value, $E_{pitting}$.](image)
its lowest value with the addition of 25 ppm, 8 × 10⁻³ mA/cm², much lower than 1 × 10⁻³ mA/cm² as reported in the literature (32–35): on the other hand, the Eₚᵣᵣ value increased with the inhibitor concentration, reaching its highest value at this inhibitor concentration also. Both the anodic and cathodic Tafel slopes were affected by the inhibitor, although in a more marked way the cathodic slope, indicating that it is acting as a mixed type of inhibitor, affecting both the anodic and cathodic reactions. Thus, the addition of the inhibitor into the H₂S-containing solution not only decreased the corrosion current density of the super martensitic stainless steel, but also the passive film properties, such as the Iₚₐₛₐₛ and Eₚᵣᵣ values were improved. This is because metal ions (Mⁿ⁺) such as Fe²⁺, Cr³⁺, Ni²⁺ and Mo²⁺ react with the inhibitor to form a complex, [Mⁿ⁺⁻Inh]ₐₜ₅ which is adsorbed and incorporated into the passive film to protect the metal from further corrosion (9, 12, 13).

### 3.4. Linear polarization resistance measurements

The change in the polarization resistance value (Rₚ) with time at different inhibitor concentrations for the UNS S41425 type super martensitic stainless steel in the H₂S-containing NaCl solution is given in Figure 7. Corrosion current density values, Iₗₜₜₜ, can be calculated by using the Stern-Geary equation:

\[ I_{corr} = K/R_p \] (2)

where \( K = (\beta_a \beta_c)/2.23(\beta_a + \beta_c) \), and \( \beta_a \) and \( \beta_c \) the anodic and cathodic Tafel slopes respectively. For the blank, uninhibited solution, where the lowest Rₚ values were obtained, and, according to eq. (2) the highest \( I_{corr} \) values, the Rp value decreased as time elapsed, indicating an increase in the \( I_{corr} \) values, due to the non-protective nature of the formed corrosion products. As soon as the inhibitor was added, the Rₚ value increased, reaching its highest value for an inhibitor concentration of 25 ppm, decreasing with a further increase in the inhibitor concentration. For a given inhibitor concentration, the \( R_p \) value increased monotonically with time until it reached a maximum value, and it decreased once again for a further increase in the elapsing time. This monotonic increase in the \( R_p \) value with time is due to an increase in the metal surface area covered by the inhibitor and indicates the protective nature of the corrosion products formed on top of the metal surface, whereas the observed drop can be due to a desorption of the corrosion products (29).

By using the \( R_p \) values, it was possible to calculate the I.E. values by suing equation:

\[ \text{I.E.} (\%) = 100 \frac{(R_{p1} - R_{p2})}{R_{p1}} \] (3)

where \( R_{p1} \) is the polarization resistance with inhibitor and \( R_{p2} \) the polarization resistance without inhibitor. Since we are assuming that the decrease in the corrosion current density values is due to the adsorption of the inhibitor, it is necessary to know some more about the way the inhibitor is adsorbed. By using these inhibitor efficiency values obtained at the end of the experiment, several adsorption isotherms were calculated (Temkin, Frumkin and Langmuir isotherm), but, as shown in Figure 6, the best fitting was obtained with the Lagnmuir type of isotherm. Lagnmuir isotherm is given by:

\[ \frac{C_{inh}}{q} = \frac{1}{K_{ads} \theta + C_{inh}} \] (4)

where \( \theta \) is the metal surface covered by the inhibitor, \( C_{inh} \), the inhibitor concentration and \( K_{ads} \) is the equilibrium constant of adsorption process. From Figure 8, the calculated equilibrium constant \( K_{ads} \) was determined as 2.27. The equilibrium adsorption constant, \( K_{ads} \), is related to the standard free energy of adsorption (\( \Delta G_{ads}^0 \)) according to the following equation:

\[ \Delta G_{ads}^0 = -RT \ln (10^6 K_{ads}) \] (5)

where \( R \) is the universal gas constant, \( T \) is the absolute temperature, and 106 is the concentration of water in the solution in mg/L. This leads to an adsorption free-energy value of -24.5 kJ mol⁻¹. Generally, values of the adsorption free-energy around -20 kJ mol⁻¹ have typically been correlated with the electrostatic interactions between organic molecules and charged metal surface (physisorption) whilst those values in the order of -40
kJ mol\(^{-1}\) are associated with charge sharing or transfer from the organic molecules to the metal surface (chemisorption) to form a coordinate type of bond \((16, 18)\). The negative value of the free-energy of adsorption value means that the adsorption process is spontaneous, while the value around \(-20\ \text{kJ mol}^{-1}\) indicates that bis(2-((2-palmitoamidoetil) amino) etil) \(1H\)-imidazol-4,5-dicarboxilate was physically adsorbed on the steel surface.

### 3.5. EIS measurements.

Nyquist and Bode diagrams for the UNS S41425 type supermartensitic stainless steel in the \(\text{H}_2\text{S}\)-containing \(\text{NaCl}\) solution containing different concentrations of bis(2-((2-palmitoamidoetil) amino) etil) \(1H\)-imidazol-4,5-dicarboxilate is given in Figure 9. From Nyquist diagrams shown in Figure 9 a, it is clear that data display, at all frequency values a single capacitive, depressed loop, which indicates that the corrosion process is under charge transfer control. The loop diameter increases as the inhibitor concentration increases, reaching its highest value with an inhibitor concentration of 25 ppm, decreasing when the inhibitor concentration increases to 50 and 100 ppm. On the other hand, Bode diagrams, Figure 9 b, indicates that the impedance value reaches its maximum value at an inhibitor concentration of 25 ppm, increasing from a values of 100 ohm cm\(^2\) obtained in the uninhibited solution up to a value higher than 7,000 ohm cm\(^2\) at 25 ppm, which is due to the adsorption of the inhibitor on the metal surface \((46, 47)\). This increase in the impedance value in presence of the inhibitor is due to the formation of a protective layer due to the reaction of the inhibitor and metal ions released during the corrosion reaction. The Bode plots in the phase angle mode shows only one peak for the uninhibited solutions, with a phase angle close to 70\(^\circ\), indicating the absence of any protective layer and the presence of one capacitive time constant, indicating that only one phenomenon is happening. The absence of linear log Z relations with a slope of \(-1\) (especially in the case of an uninhibited system) and the departure of phase angle at intermediate frequencies from 90\(^\circ\) shows that the system tends to the resistive behavior. However, as the inhibitor concentration increases, the phase angle approaches to 80\(^\circ\) the frequency interval where phase angle remains constant is broader, which is due to the existence of two overlapped peaks, indicating a passive film acting as an insulator, suggesting that a highly stable film is formed on top of the tested metal in the electrolyte used. EIS data were simulated by using electric circuits given in Figure 10. In these figures, \(R_s\) is the solution resistance, \(R_{ct}\) the charge transfer resistance and \(R_f\) is the resistance of the protective film, whereas \(C_{dl}\) and \(C_f\) are the double layer and film capacitance values respectively. The fact
that in the Nyquist plots the loops are depressed due to surface heterogeneities and that the linear part of the impedance-logarithm of the frequency has a slope value different from $-1$, indicates that they deviate from an ideal behavior of a double layer capacitance. In this case, capacitances, i.e. $C_{dl}$ and $C_f$ are replaced by constant phase elements, CPE, which has an impedance value, $Z_{CPE}$:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (6)$$

A parameter which provides csuch as roughness. Parameters obtained for fitting EIS data by using electric circuits shown in Figure 10, Table 3, indicate that the film resistance values, $R_f$, are much higher than those for the charge transfer resistance values, $R_{ct}$, which indicates that the steel corrosion resistance is given by the formed film on top of the steel rather than by the double electrochemical layer resistance. In addition to this, we can see that as the $R_f$ value increases whereas the value for $C_f$ decreases with the inhibitor concentration, at least up to a concentration of 25 ppm. After this concentration the opposite is observed. This has been attributed to the adsorption of organic molecules of the inhibitor which replace the water molecules from the steel. By using the Helmholtz model and the standard formula for conventional plate capacitors, the decrease in $C$ can be related to an increase in double-layer thickness, as a result of the inhibitor adsorption, capacitance can be calculated by using:

$$C_{dl} = \varepsilon \varepsilon_0 A / \delta \quad (7)$$

where $C_{dl}$ is the double layer capacitance, $\delta$ the double layer thickness, $\varepsilon$ is the double layer dielectric constant, $\varepsilon_0$ the vacuum electrical permittivity, and $A$ the surface area. Thus, the decrease in the capacitance value is due to the adsorption of the inhibitor which has a lower dielectric constant value or to a lower value for $A$ where the charge transfer reaction occurs.

### 3.6. SEM studies

The corroded surfaces of UNS S41425 type super martensitic stainless steel in the H$_2$S-containing NaCl solution containing 0 and 25 ppm of inhibitor are given in Figure 11, whereas a chemical analysis of the corrosion products are given in Figure 12. It can be seen that for

![Figure 10. Electric circuits to simulate EIS data for UNS S41425 type supermartensitic stainless steel corroded a H$_2$S-containing solution a) in absence and b) presence of bis(2-(2-palmitoamidoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate.](image1)

![Figure 11. SEM micrograph of UNS S41425 type supermartensitic stainless steel corroded a H$_2$S-containing solution containing a) 0 and b) 25 ppm of bis(2-(2-palmitoamidoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate.](image2)

| $C_{inh}$ (ppm) | $R_s$ (ohm m$^2$) | $C_{dl}$ ($\mu$F cm$^{-2}$) | $R_{ct}$ (ohm m$^2$) | $C_f$ ($\mu$F cm$^{-2}$) | $R_f$ (ohm m$^2$) |
|-----------------|------------------|-------------------|---------------------|-------------------|------------------|
| 0               | 3                | 539               | 123                 | —                 | —                |
| 5               | 2                | 105.7             | 150                 | 104.5             | 459              |
| 10              | 4                | 48.2              | 235                 | 49.2              | 1572             |
| 25              | 2                | 21.7              | 356                 | 12.4              | 7219             |
| 50              | 3                | 32.8              | 135                 | 19.1              | 6708             |
| 100             | 3                | 56.3              | 45                  | 40.5              | 3976             |

Table 3. Electrochemical parameters to fit the EIS data of UNS S41425 type supermartensitic stainless steel corroded a H$_2$S-containing solution containing different concentrations of bis(2-((2-palmitoamidoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate at 50°C.

Figure 11.
the specimen corroded in absence of inhibitor, Figure 11 a, the layer of corrosion products presented numerous cracks, which are natural paths for the corrosive environment to penetrate and corrode the underlying metal. On the other hand, the corrosion products formed on top of the metal corroded in presence of inhibitor, Figure 11 b, the corrosion products layer is more compact but they still present some cracks, and, therefore, the corrosive environment can still penetrate and corrode the underlying metal, explaining why the inhibitor efficiency did not reach 100% as shown in Table 4. Chemical analysis for both layers of corrosion products, Figure 12, indicates the presence of the elements present in the alloy, i.e. Fe, Cr, Ni, Mn, C and Si, together with some elements present in the solution such as S and Na, suggesting that maybe the main compounds should be sulfides and, probably some oxides as reported in earlier works (33, 38, 45); the presence of Mo in these corrosion products layer

Table 4. Electrochemical parameters obtained from the polarization curves of UNS S41425 type supermartensitic stainless steel corroded a H2S-containing solution containing different concentrations of bis(2-((2-palmitoamidoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate at 50°C.

| C_{inh} (ppm) | $E_{corr}$ (mV) | $I_{corr}$ (mA/cm²) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | I.E. | $E_{pit}$ (mV) | $I_{pas}$ (mA/cm²) |
|---------------|----------------|---------------------|-------------------|-------------------|-----|-------------|----------------|
| 0             | $-520 \times 10^{-4}$ | 95                  | 420               | --                | --  | $-85 \times 10^{-4}$ | 7 × 10^{-4} |
| 5             | $-460 \times 10^{-5}$ | 90                  | 175               | 91                | 0.91 | $-60 \times 10^{-4}$ | 5 × 10^{-4} |
| 10            | $-445 \times 10^{-6}$ | 85                  | 200               | 97                | 0.97 | $-40 \times 10^{-5}$ | 2 × 10^{-4} |
| 25            | $-435 \times 10^{-6}$ | 110                 | 160               | 99                | 0.99 | $-6 \times 10^{-5}$ | 8 × 10^{-5} |
| 50            | $-455 \times 10^{-6}$ | 140                 | 150               | 98                | 0.98 | $-25 \times 10^{-5}$ | 5 × 10^{-4} |
| 100           | $-445 \times 10^{-6}$ | 90                  | 175               | 98                | 0.98 | $-50 \times 10^{-5}$ | 2 × 10^{-4} |

Figure 12. EDX microchemical analysis of corrosion products for UNS S41425 type supermartensitic stainless steel corroded a H2S-containing solution containing a) 0 and b) 25 ppm of bis(2-((2-palmitoamidoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate.
was not found, indicating, as suggested somewhere else (36–38) that it went directly into the solution. Some researchers have suggested that the Sulfide stress cracking and pitting resistance of supermartensitic stainless steels in sulfide environments is due to the formation of Mo sulfides on the external part of the corrosion products layer and that it can assist for the formation of a chromium oxide layer in the internal part of this layer (3, 50, 51). However, Mo was not detected as part of the corrosion products external layer in our case, and, as suggested somewhere else, it is because Mo, during the dissolution process, goes into the solution directly without forming part of the layer formed on top of the steel.

4. Conclusions

Our results have shown that namely bis(2-((2-palmitoa-midoetil) amino) etil) 1H-imidazol-4,5-dicarboxilate acts as an efficient corrosion inhibitor for UNS S41425 type supermartensitic stainless steel in presence of H2S. Polarization curves have shown that the inhibitor efficiency increased with its concentration up to 25 ppm, but it decreased with a further increase in its concentration. Inhibitor affected both anodic and cathodic electrochemical reactions, improving the passive film properties. LPR measurements have indicated that inhibitor was physically adsorbed on to the steel surface by following a Langmui type of adsorption isotherm, but after a few hours, it was desorbed from the steel surface.

Disclosure statement

No potential conflict of interest was reported by the authors.

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