(2S,3R)-2-((1-(4-amionophenyl) ethylidene)amino )-3-hydroxybutanoic acid as a novel and eco-friendly corrosion inhibitor for the carbon steel (X56) used in Iraq's oil installations

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ABSTRACT

Herein, the successful a novel corrosion inhibitor ((2S,3R)-2-((1-(4-amionophenyl) ethylidene) amino) -3-hydroxybutanoic acid compound (S1 ) was synthesized by the condensation reaction of equimolar of the 4-amino acetophenone with threonine amino acid. °H NMR, 13C NMR ,C.H.N., and FTIR techniques were used to confirm the structure of the S1 inhibitor. The impacts of S1 inhibitor was tested on the carbon steel (x56) in 0.5 N hydrochloric acid solution at 298.15 K. The electrochemical measurements were accomplished such as open circuit potential (OCP) and polarization scan, the results were confirmed the S1 as an excellent inhibitor and act as a mixed inhibitor to control on both the anodic and cathodic reaction to retarding the corrosion process by blocking the active sites on the surface electrode. These data were proved by the FE-SEM images and mapping spectra, it was seen the protective layer clearly on the surface.

Keywords: corrosion inhibitor, polarization, Tafel, and carbon steel.
Introduction

Corrosion is the process that converts metal into a chemically stable configuration like hydroxide, oxide, and sulfide[1]. This process happens with the gradual destruction of the materials via an electrochemical reaction chemical or chemical with their environment[2–4]. The metal parts used in industry are subject to rapid corrosion, which greatly increases both scheduled and unplanned maintenance costs[5,6]. Corrosion-resistant steel has attracted great interest in industrial application as a way to reduce costs associated with product failure[7]. As the increased corrosion resistance of the metals extends the life of metal parts and thus reduces replacement and maintenance costs[8]. For that, no cost-effective process has been developed to produce highly corrosion-resistant metals for use in the manufacture of steel products[9]. Corrosion in the oil industries is one of the central and dangerous constraints that accompany these industries, starting from the extraction of crude oil and ending with the stages of the use of its derivatives, through purification, refining, manufacturing, and transportation, and storage operations. Refinery equipment and metallic constructions in oil refineries and petrochemical mills are in contact with the ore oils and fuel and products of petroleum, solvents, soil, atmosphere, and water[10–12]. The acidic solutions are the most corrosive mediums and used in conserve, acid cleaning, sediment boiler, and oil well industries[7,13,14]. The essential criteria adopted in selecting the appropriate inhibitors depend mainly on the type of acid, concentration, and temperature. Some organic derivatives of amino acids were investigated by researchers as corrosion inhibitors for the carbon steel in acidic solutions such as hydrochloric acid[15–17].

The inhibition process occurs via the electrostatic interactions molecules and the interaction between unshared electron pairs of hetero-atoms and vacant d-orbital of iron surface atoms[18,19]. The non-toxic of various amino acid derivatives as threonine has led to their use as corrosion inhibitors due to the presence of electrons and heterogeneous atoms as well as aromatic rings in their structures that absorb or form an insoluble metal compound on the surface of the metal[20–22]. So, the present work aims to study the inhibition effect of (2S,3R)-2-((1-(4-amionophenyl) ethyldene)amino ) -3-hydroxybutanoic acid on the corrosion of carbon steel type X56 in 0.5 N HCl aerated solution. The chemical structure of the corrosion inhibitor used in this study, as shown in Fig. 1.
Fig. 1: Chemical structure of (2S,3R)-2-((1-(4-amionophenyl) ethylidene)amino) -3-hydroxybutanoic acid

2: Experimental setup

2:1: Materials and solutions

The Carbon steel (X56) coupon was taken from Iraq’s oil refine fields and had the compositions of the following elements, as shown in Table 1. The optical emission spectroscopy type PMI MASTER PRO2 used to reveal the chemical structures of the MS specimen. The appropriate sample was prepared with dimensions (1 cm × 1 cm) and thickness (0.4 cm). All carbon steel (X56) specimens polished like a mirror by using the emery papers at different sizes and finally by the soft cloth with diamond past as lubricating oil.

| Elements | C   | Mn  | Si   | S    | P    | Ni   | Cu   | Fe   |
|----------|-----|-----|------|------|------|------|------|------|
| Wt %     | 0.174 | 1.36 | 0.367 | 0.0035 | 0.0116 | 0.033 | 0.012 | Balance |

To prepare the working carbon steel electrode, it was covered with an epoxy resin, for that the exposed area 1 cm2 to contact with the electrolyte solution[23]. All of the experiments were achieved in the temperature 303.15 K which freshly prepared with deionized water, in 0.5 normal of hydrochloric acid (which was purchased from the Sigma-Aldrich com. LTD) solution in the presence the of carbon dioxide gas. To study the inhibitor effects of (2S,3R)-2-((1-(4-amionophenyl) ethylidene)amino) -3-
hydroxybutanoic acid compound as a corrosion inhibitor, prepared various concentrations (10, 30, and 50) ppm in 0.5 N HCl aggressive aerated acidic media.

2:2: Synthesis of corrosion inhibitor

A novel (2S,3R)-2-((1-(4-amionophenyl) ethylidene)amino) -3-hydroxybutanoic acid compound (S1) was synthesized by the condensation reaction of equimolar from the 4-amino acetophenone (1mmol) with threonine amino acid (1mmol) in 25 mL mixture of absolute ethanol and sodium hydroxide[24]. The mixture was reflexed for 55°C for 10 h under magnetic stirred to give a yellow color, this is the first identify to formation the Schiff base. Moreover, the progress of the reaction was followed up by the thin film chromatography (TLC). The solution obtained was evaporated under 25°C. The solid obtained was washed several times with absolute ethanol, and then recrystallized by utilized the deionized water-ethanol mixture (1:3). The S1 compound (product yield 86%) was prepared to record the melting point in the range 199-201°C. To estimate the purity of the S1 compound, 1H NMR, 13C NMR, C.H.N., and FTIR measurements were used to the characterized structure of the ((2S,3R)-2-((1-(4-amionophenyl) ethylidene)amino) -3-hydroxybutanoic acid corrosion inhibitor.

2:3: Electrochemical measurement

The corrosion cell was constructed with carbon steel (X56) as the working electrode to study the inhibitory effects of (2S,3R)-2-((1-(4-amionophenyl) ethylidene)-3-hydroxybutanoic compound on the corrosion of the carbon steel (X56) when exposed to the aerated hydrochloric acidic solution (0.5 N) in the 303.15 K. The Calomel and Platinum electrodes were used as a reference and auxiliary electrodes, respectively. All of them were placed in corrosion electrochemical cell in the same time and connected with the M-lab Potentiostat/Galvanostat device (BANK ELETTRONIC company, Germany) to measure the polarization curves and estimated the parameters of corrosion process such as the corrosion current density (icorr), corrosion potential (Ecorr.), anodic and cathodic Tafel slopes (βa,βc), respectively, and the corrosion rate at the polarized carbon steel (X56) working electrode.

2:4: Characterization techniques

Carbon steel (X56) specimens were characterized by the field emission scanning electron microscope (FESEM) ZEISS Gemini type 500 (ZEISS, Germany LTD. company) at the accelerating voltage (0.02 - 30) k and the magnification of image (50 – 2,000,000). Firstly, the carbon steel (X56) sample (exposed area ~ 1.8 cm2) was
immersed in the 75 mL test solution of 0.5 N HCl. Thus, 50 ppm of S1 inhibitor concentration was prepared in the same first test solution at the 303.15 K for the 24 h. The FESEM images were taken to study the morphology of carbon steel surface in with and without the inhibitor. EDS (energy dispersive spectroscopy) spectrums were determined to identify the compositions of the chemical elements at the same conditions of the aggressive electrolyte solution. It is necessary before each image was recorded, the samples were washed with deionized water and dried in a desiccator for one hour.

### 3: Results and discussion

The synthesis steps and the suggested mechanism of studied (2S,3R)-2-((1-(4-amionophenyl) ethylidene)amino)-3-hydroxybutanoic acid (S1) compound as a corrosion inhibitor is illustrated in scheme.1

![Scheme 1: The suggested mechanism of the S1 corrosion inhibitor.](image)

The product yield is 86% of the yellow solid. The results of the $^1$H NMR were recorded as the following signals (D$_2$O, δ ppm): 1.1 (6H, 1, H-2,14),6.7 (2H, d, H-
7.5', 7.7 (2H, d, H-4,8'), 4. (3H, s, H-12), 4.59(2H, s, H-N'), 3.4 (1H, m, H-OH ),2.4 (1H, m, H-15 ), 3 (1H, f, H-13 ) (Fig. 2 )and $^{13}$C NMR : 177(C-10'), 69 (C-12), 114 (C-5,7),62 (C-13),131(C-3,4,8) as shown in Fig. 3. Furthermore, C.H.N. elemental analysis technique was recorded for the S1 corrosion inhibitor, and the results gave the ratio of carbon: nitrogen of 4.405 with the percentage of content elements N (11.01), C(48.51), S(6.251), and H(4.137).

Fig. 2: $^1$H NMR spectrum of the S1 compound as the corrosion inhibitor.
The FT-IR spectra (KBr, $v_{max}$ cm$^{-1}$) of S1-(2S,3R)-2-((1-(4-aminophenyl)ethylidene)amino)-3-hydroxybutanoic acid compound as shown in Fig. 4 a,b. In figure 4a bonding configurations of S1 have been obtained from the characteristic peaks in FT-IR spectra. The peak at 3226 and 2960 cm$^{-1}$ refers to the N–H stretching vibration and the sp$^3$ C-H stretching vibration, respectively. The band at 3040 can be ascribed to the C-H aromatic stretching vibration of the benzenoid ring. The boarding band at 3300 cm$^{-1}$ in the FT-IR spectra of S1 is the characteristics of O–H stretching vibrations. Also, the bands at 3386, and 1650 cm$^{-1}$ can be assigned to the 2N-H stretching vibration and the C=N for stretching vibration of the amide bond. Moreover, In figure 4b bonding configurations of S1 after the immersion of the carbon X56 sample in 0.5 N in an aerated hydrochloric acidic solution for the 24 h has been obtained from the characteristic peaks in FT-IR spectra. The peaks at 3226, 2961, and 3058 cm$^{-1}$ refers to the N–H stretching vibration, sp$^3$ C-H bond, and C-H aromatic stretching vibration, respectively. The bands at 3420 and 3386 cm$^{-1}$ can be ascribed to the O-H stretching vibration of the benzenoid ring and 2N-H stretching vibration, respectively. The strong bands at 1731 cm$^{-1}$ in the FT-IR spectra of S1 are the characteristics of C=N stretching vibrations. For that, The bands that appeared in figure 4b were shifted due to the adsorption process which happens to absorb the S1 inhibitor on the carbon steel surface.
Fig. 4: FT-IR spectrum of the S1 compound as the corrosion inhibitor before immersion (a), after the immersion in 0.5 N HCl

It is essential to study the open circuit potential (OCP) before recorded the Potentiodynamic measurements (polarization curve). For that, the measured of OCP values of carbon steel (X56) electrode in 0.5 N HCl aerated solution as a function of the time. In other words, the OCP information provides an idea of the anodic and cathodic procedure for the corrosion process. The OCP is a steady-state potential at which an X56-working electrode equilibrates in a given acidic solution without an external source shifting the voltage (potential value) from the equilibrium state (value)[25]. Fig. 5 illustrates the fluctuation of the open circuit potential of the X56 working electrode with interval time in 0.5 normal hydrochloric acid solution in the absence and the presence of S1 corrosion inhibitor at the 289.15 K. It can be seen that the curve of OCP drifts towards more negative values and which led to a short step. This behavior was studied by the West and co-workers[21,26], which denotes the collapse of the oxide film formed in the air before immersion displays on the working electrode surface, as shown in the following equation: \( \text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \) .... (1).
Fig. 5: OCP curves of X56 carbon steel in 0.5 N HCl solution at different concentrations. (a) blank, (b) 10, (c) 30, and (d) 50 ppm.

Moreover, in the presence of the S1 inhibitor, the OCP potential values shifted towards a more positive direction, especially in a high concentration of inhibitor (50 ppm). This happening can be interpreted in the idea of the formation of the protective film on the surface carbon steel (X56). For that, at a high concentration established of the steady iron $\text{Fe}^+–$ complexes alongside nitrogen atoms[27].

Fig. 6: Polarization curves of the carbon steel X56 working electrode in 0.5 N HCl, (a) blank, (b) 10, (c) 30, and (d) 50 ppm.

As cited in the OCP electrochemical measurements, there is attention was taken to the stability of the OCP value before the polarization scan was recorded. To know more
about the kinetics of the corrosion reaction, which includes both the anodic and cathodic reactions that happen on the X56 working electrode surface, the carbon steel sample was immersed in the 0.5 N hydrochloric acid solution in the absence and presence of the S1 inhibitor at 289.15 K. The information obtained from the potentiodynamic scan are shown in Fig.6. The full parameters of the polarization curves such as the corrosion potential, corrosion current density, Tafel constants, the corrosion rate, and inhibition efficiency are tabulated in Table. 2. It can be observed that the corrosion potentials ($E_{corr}$) shifted to a more negative with the S1 corrosion inhibitor, this result has affirmed the influence of the S1 compound as an organic inhibitor in retarding the $E_{corr}$ by the adsorption process and hence blocking the active area sites on the X56 surface electrode. From Table.2, the corrosion current density ($i_{corr}$) decreased significantly and a grater drift is observed at the concentration of 30 ppm and the inhibition efficiency ($P\%$) is 74.09. The $P\%$ values that mentioned in table 2, were estimated via the equation: $P\% = \left( \frac{i_{corr\ blank} - i_{corr\ S1}}{i_{corr\ blank}} \right) \times 100$. The variation of the cathodic ($b_c$)and anodic ($b_a$) Tafel slope constants were perceived as the concentration of S1 inhibitor was a varied significant change in $b_c$ Tafel constants. The slightly changed an anodic slope constant ($b_a$) which demonstrates interference in the mechanism of corrosion reaction in the presence of S1 inhibitor.

**Table 2:** Polarization curve parameters with the inhibition efficiency of the X56 working electrode in the 0.5 N HCl solution at 298.15 K at different concentrations.

| S1 inhibitor | $i_{corr} \times 10^{-6}$ µA/cm² | -$E_{corr}$ mV | $b_c \times 10^{-3}$ V/decade | $b_a \times 10^{-3}$ V/decade | Corrosion Rate/mpy | $P\%$ |
|--------------|---------------------------------|----------------|-------------------------------|-------------------------------|-------------------|-------|
| Without S1  | 583.0                           | 481.0          | 115.6                         | 80.90                         | 266.3             | -     |
| 10 ppm       | 413.0                           | 510.0          | 123.0                         | 74.70                         | 188.8             | 29.15 |
| 30 ppm       | 232.0                           | 503.0          | 132.4                         | 77.30                         | 106.2             | 60.20 |
| 50 ppm       | 151.0                           | 528.0          | 155.3                         | 83.90                         | 69.04             | 74.09 |

These data indicate that the corrosion inhibitor (S1) acts as a mixed type inhibitor with main control on the cathodic reaction by retarding the evolution of hydrogen via the blocking effect of the active sites.
Fig. 7: FE-SEM images (A) and Mapping spectra (B and C) for the X56 surface electrode in 0.5 N HCl after immersion in the presence of S1 corrosion inhibitor at 298.15 K.

The values of P% were increased with increasing the concentration of S1 inhibitor in the corrosive HCl solution, as shown in Table 2. This it might interpret that the corrosion inhibitor S1 is a good inhibitor, especially at a high concentration to control the corrosion process and leads to an increase in the inhibition efficiency values. This behavior is consistent with decreasing the corrosion rate from 266.3 to 69.04 mpy. The FE-SEM technique was used to characterize the surface of the carbon steel X56 in 0.5 hydrochloric acids aerated solution in the presence of an S1 inhibitor at 298.15 K, as shown in Fig. 7 a,b, and c. The surface of the electrode seems to have sustained less damage in the aggressive HCl solution, due to the disappearance of the cracking and pitting with the formation of the pale grey thin film (Fe3C film)[21,28]. There is emphasized on the protective film layer (Fig. 7 a) on the X56 surface electrode and this an improvement in the integrity of the carbon steel surface. Moreover, the mapping results have given the composition of the analysis of the elements of the protective layer, it seems that the elements as carbon, oxygen, nitrogen, and iron are present, as displayed in Fig 7 b and c. For that, the aggressive attack seems less severe in the presence of an S1 compound as a corrosion inhibitor.
4: Conclusion

In the present work, we successfully to synthesis a novel corrosion inhibitor (2S,3R)-2-((1-(4-amionophenyl) ethylidene)amino ) -3-hydroxybutanoic acid compound (S1) via condensation reaction of equimolar of the 4-amino acetophenone with threonine amino acid. ¹H NMR, ¹³C NMR ,C.H.N., and FTIR techniques were used to confirm the structure of the S1 inhibitor. The carbon steel type x56 was used as a working electrode to test the S1 inhibitor in 0.5 N hydrochloric acid solution at 298.15 K. The electrochemical measurements were achieved such as open circuit potential and polarization scan, the results were affirmed the S1 as an excellent inhibitor and act as a mixed inhibitor to control on both the anodic and cathodic reaction to retarding the corrosion process by blocking the active sites on the surface electrode. These data were proved by the FE-SEM images and mapping spectra, it was seen the protective layer clearly on the surface.

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