

## Study of the inhibition of corrosion of mild steel in a 1M HCl solution by a new quaternary ammonium surfactant

O. Abdellaoui<sup>a</sup>, M.K. Skalli<sup>a</sup>, A. Haoudi<sup>a</sup>, Y. Kandri Rodi<sup>a</sup>, N. Arrousse<sup>b</sup>, M. Taleb<sup>b</sup>, R. Ghibate<sup>c</sup>, O. Senhaji<sup>c\*</sup>

<sup>a</sup>Laboratory of Applied Organic Chemistry, Faculty of Science and Technology, B.P. 2202, Fez, Morocco

<sup>b</sup>Laboratory of Engineering, Electrochemistry, Modeling and Environment, Faculty of Sciences, Dhar El Mahraz, B.P. 1796 Fez-Atlas, Morocco.

<sup>c</sup>Team of Biomolecular and Macromolecular Chemistry, Faculty of Sciences, B.P. 11201 Zitoune Meknes, Morocco.

### Abstract

The anticorrosive effect of surfactant, 12-(2,3-dioxindolin-1-yl)-N,N,N-trimethyldodecan-1-ammonium bromide **3** on the corrosion of mild steel in 1M hydrochloric acid was assessed by gravimetric and electrochemical techniques (potentiodynamic polarization and electrochemical impedance spectroscopy). The results have shown that our synthesized surfactant is an excellent corrosion inhibitor for mild steel in 1 M HCl. Inhibitory efficacy of up to 95.9% was exhibited by surfactant **3** at a concentration of 1 mM after 6 h immersion at 298K. Based on the polarization curves, it is clear that the surfactant **3** can be considered as a mixed inhibitor with a predominantly anodic character. The inhibitory effectiveness increases with increasing concentration but decreases with increasing temperature. It was found that the adsorption of the inhibitor on the surface of the mild steel in 1M HCl followed the Langmuir adsorption isotherm. In this context, the main kinetic and thermodynamic parameters were determined and discussed.

\* Corresponding author:

[o.senhaji@umi.ac.ma](mailto:o.senhaji@umi.ac.ma)

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## 1. Introduction

Mild steel is a preferred material in many industries. Its excellent mechanical properties and low cost make it widely used as a building material for piping and in oil and gas production, such as conduit tubes, downspouts, and transport tubes [1–3]. However, mild steel has suffered from corrosion attack in industrial applications, in particular from the hydrochloric acid attack, which is widely used in the industry for acid cleaning, descaling, pickling, etc [4–7]. Nevertheless, its sensitivity to corrosion remains a major constraint to its use. The most frequent method for retarding metal corrosion is the use of corrosion inhibitors as it requires no special equipment, is inexpensive and easy to use [8,9]. The majority of inhibitors destined for this use are organic compounds, which possess coordination sites to coordinate with metals. Such sites of coordination may contain multiple bonds and heteroatoms like nitrogen, sulfur, and oxygen [10,11]. These inhibitors reduce corrosion by blocking the active corrosion sites and form a protective layer by complexing on the metal surface. They act mainly by adsorption phenomena (chemisorption and/or physisorption) due to the interaction of the active sites located on the surface of the metal with the molecular structures of the inhibitor. The density and availability of free pi  $\pi$  electrons on the functional groups of inhibitor compounds generally control the intensity of the interaction [12,13]. Overall, numerous inhibitors of corrosion present problems for the environment because of their toxicity. New corrosion inhibitors should be non-toxic and respectful of the environment [8,14]. In the last years, considerable efforts have been made to find new anti-corrosive organic molecules, and N-heterocyclic Compounds were found to be effective corrosion inhibitors [15–17]. One choice would be a compound based on the indole; Indole and its derivatives have important functionalities due to their ability to interact strongly with the metal surface, also there are widely used in the medical field they have antimicrobial [18]; anticancer [19]; antifungal [20]; anti-inflammatory [21]; and anti-tuberculous activities. Several isatin derivatives (indol-2,3-dione) have been proposed as efficient corrosion inhibitors for copper [22], aluminum [23], and steel [24,25]. Besides, the use of surfactants in an acidic medium is an effective and relatively inexpensive method of preventing corrosion of metallic surfaces. Surfactants have been applied to electroplating ventures for their diverse benefits. The advantages of surfactants are many, such as high inhibition effectiveness, low toxicity, low cost, and ease of production [26–29]. The aim of this work was to synthesize a surfactant derived from isatin and to study their anti-corrosive properties of mild steel in a 1 M HCl medium. The detailed study of the surfactant was carried out using weight loss, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization methods. The corrosion inhibition mechanism and the mode of adsorption of inhibitor compound on mild steel were also assessed.

## 2. Experimental details

### 2.1. General procedures for the synthesis of inhibitor (compound 3)

The inhibitor was synthesized by alkylation reaction of isatin under phase-transfer catalysis conditions followed by a quaternization reaction of the alkylated product with trimethylamine.

#### 2.1.1. Synthesis procedure for compound 2

A mixture of isatin (1g, 6.796 mmol), potassium carbonate (1.4 g, 10.129 mmol), 1,12-dibromododecane (2.68g, 8.167 mmol), tetra-n-butylammoniumbromide (0.24 g, 0.745 mmol), in DMF (40 mL) was stirred for 48 hours at room temperature. After filtration of the reaction mixture, the solvent was removed under vacuum and the raw product purified by chromatography column.

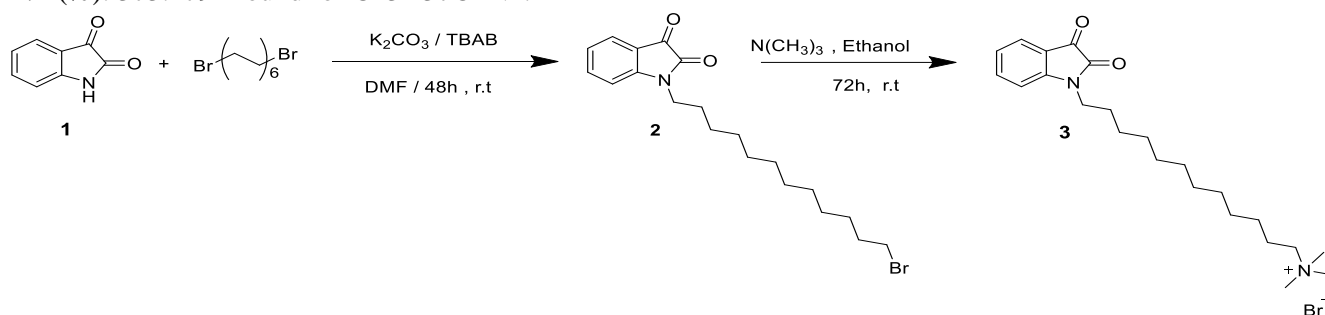
Yield 78 %; Mp 61 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>; 300MHz);  $\delta$ (ppm), 1.4 (m, 16H, CH<sub>2</sub>); 1.7 (q, 2H, CH<sub>2</sub>CH<sub>2</sub>N, 3JH-H= 7,5Hz); 3.4 (t, 2H, CH<sub>2</sub>Br, 3JH-H= 6,9Hz); 3.7(t, 2H, NCH<sub>2</sub>, 3JH-H= 7,5Hz); 6.9 (d, 1H, CHAr,3JH-H= 8,1Hz) ;

7.1 (t, 1H, CHAr, 3JH-H= 7,5Hz); 7.6 (m, 2H, CHAr).  $^{13}\text{C}$  NMR(CDCl<sub>3</sub>; 75MHz);  $\delta$ (ppm): 26.87; 27.24; 28.14; 28.73; 29.19; 29.37; 29.42; 29.44; 32.81; 34.07; 40.26; (CH<sub>2</sub>); 110.18; 123.58; 125.40; 138.32; (CHAr); 117.59; 151.08; (Cq); 158.12 (N-C=O). HRMS (EI) m/z (%): 394.1329 found for C<sub>20</sub>H<sub>28</sub>O<sub>2</sub>NBr<sup>+</sup>H<sup>+</sup>.

### 2.1.2. Synthesis procedure of inhibitor 3

In a two-necked flask attached to a reflux condenser, trimethylamine (31- 35% w/w) (3.3mL; 12.98 mmol) was added dropwise to 1-(12-bromododecyl) indoline-2,3-dione **2** (1g; 2.536 mmol) solubilized in 40 mL ethanol. After stirring the reaction 72h at room temperature, the solvent removed under vacuum and the crude product solubilized in the minimum of ethanol then precipitated in ether to produce an orange solid with 96 % yield.

Yield 96 %; Mp 171 °C;  $^1\text{H}$  NMR (D<sub>2</sub>O; 300MHz);  $\delta$ (ppm), 1.08 (m, 16H, CH<sub>2</sub>); 1.42 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>N); 1.63 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>); 3.08 (s, 9H, CH<sub>3</sub>N<sup>+</sup>); 3.27 (t, 2H, CH<sub>2</sub>N, 3JH-H= 8.1Hz); 3.5(m, 2H, CH<sub>2</sub>N<sup>+</sup>); 6.97 (t, 2H, CHAr, 3JH-H= 7.5Hz); 7.26 (d, 1H, CHAr, 3JH-H= 7,2Hz) ; 7.53 (t, 1H, CHAr, 3JH-H= 7.5Hz).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>; 75MHz);  $\delta$ (ppm): 22.69; 26.00; 26.72; 27.13; 28.97; 29.15; 29.39; 29.45; 40.06; 61.76; 65.97; 66.47 (CH<sub>2</sub>); 53.01 (CH<sub>3</sub>N<sup>+</sup>); 111.16; 123.97; 124.90; 139.37 (CHAr); 117.01; 150.77 (Cq); 158.24 (N-C=O); 183.96(C=O). HRMS (EI) m/z (%): 373.2794 found for C<sub>23</sub>H<sub>37</sub>O<sub>2</sub>N<sub>2</sub>.



**Figure 1:** synthesis of inhibitor 12-(2,3-dioxindolin-1-yl)-N,N,N-trimethyldodecan-1-ammonium bromide **3**

### 2.2. Materials and solutions

The corrosion tests were performed on carbon steel with a chemicals compositions (in wt.%) C: 0.370, Mn: 0.230, Si: 0.680, S: 0.016, Cr: 0.077, Ti: 0.011, Ni: 0.059, Co: 0.009, Cu: 0.160 and Fe balance. The samples of mild steel used in this study were pre-treated prior the experiments by grinding with deferent emery papers sic (grade 220, 400, 800, 1000 and 1200) rinsed with bi-distilled water and degreased with acetone, and washed again with double-distilled water and then dried in air before use. All the electrochemical and gravimetric experiments were performed in HCl 1M solutions prepared by dilution of analytical solution HCl 37% with bidistilled water. The concentration range of 12-(2,3-dioxindolin-1-yl)-N,N,N-trimethyldodecan-1-ammonium bromide **3** employed was  $10^{-6}$  to  $10^{-3}$  M.

### 2.3. Gravimetric measurement

The weight loss measurements were perfected according to ASTM method. The gravimetric tests were carried out in a double glass cell equipped with a thermostat-cooling condenser. Rectangular samples with a size of 1.5 cm × 1.7 cm × 0.3 cm were immersed in 1M HCl solution in the absence and presence of various concentrations of 12-(2,3-dioxindolin-1-yl)-N,N,N-trimethyldodecan-1-ammonium bromide, for 6h at 298 K. Afterward, the steel samples were withdrawn, rinsed with bi-distilled water, degreased with acetone and finally, the specimens were dried and weighed.

## 2.4. Electrochemical studies

The electrochemical study was performed using the potentiostat PGZ 100 piloted by a software VoltaMaster 4. This potentiostat was connected to a conventional three-electrode cylindrical Pyrex glass cell. A saturated calomel electrode (SCE) was used as a reference. A platinum electrode was used as an auxiliary electrode of the surface area of 1 cm<sup>2</sup>. The working electrode was mild steel with the surface area of 1 cm<sup>2</sup>. All potentials given in this study were referred to this reference electrode. The temperature is thermostatically controlled at 298 K. The Electrochemical Impedance Spectroscopy (EIS) experiments were conducted in the frequency range of 10 mHz to 100 kHz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these measurements. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit to give the intersections with the x-axis.

## 3. Results and discussion

### 3.1. Gravimetric measurement

The gravimetric method is a simple method that does not require a large apparatus and allows to easily determining the corrosion rate and the inhibiting efficiency of an inhibitor. The evolution of the corrosion rate of mild steel as a function of inhibitor concentration was determined at 298 K, after 6 hours of immersion. The results of the corrosion rate as well as the inhibiting efficiency obtained by the gravimetric method are presented in Table 1.

**Table 1:** Corrosion parameters from weight loss measurements for mild steel after 6 hours immersion in 1 M HCl medium without and with various concentrations of surfactants at 298 K.

Concentration (M)	CR (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	IE (%)
Blank	0.480	-
10 <sup>-6</sup>	0.150	68.79
10 <sup>-5</sup>	0.058	87.86
10 <sup>-4</sup>	0.042	91.33
10 <sup>-3</sup>	0.019	<b>95.99</b>

The analysis of the results obtained showed that the increase in inhibitor concentration decreases the corrosion rate and consequently an increase in inhibitor efficiency that reaches a maximum of 95.99% at an inhibitor concentration of 10<sup>-3</sup> M. This is justified in most cases by the reason that the quantity of adsorption and inhibitor coverage on carbon steel increases with the concentration of inhibitor, which effectively protects the surface of the carbon steel from the acidic environment [30–32].

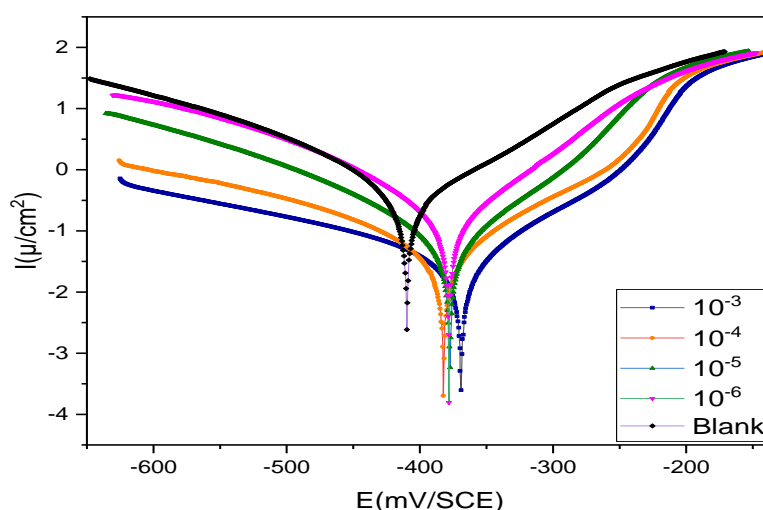
### 3.2. Polarization results

The potentiodynamic anodic and cathodic polarization curves of mild steel in the absence and presence of different concentrations of the inhibitor in an acidic 1M HCl medium were shown in Figure 2. The cathodic and anodic reactions are affected by the addition of 12-(2,3-dioxindolin-1-yl)-N,N,N-trimethyldodecan-1-ammonium bromide **3** as shown in Figure 2. As a result, the inhibitor has a tendency to reduce the metal dissolution and hydrogen evolution reactions [33,34]. As can be seen from Figure 2; that the corrosion potentials  $E_{corr}$  of the steel in the presence of the inhibitor are shifted towards positive values compared to that of the blank; this result shows that, at different concentrations, the inhibitor more affected the cathodic reaction than the anodic reaction [35,36]. Thus, the corrosion

densities  $I_{\text{corr}}$  decrease in both the anodic and cathodic regions with increasing inhibitor concentration; it can therefore be concluded that; the inhibitor is anodic of the mixed type [34,37]. The corrosion parameters are calculated from the polarization curves and shown in the Table 2 including the corrosion potential ( $E_{\text{corr}}$ ), the Tafel cathode slope ( $\beta_c$ ), the Tafel anode slope ( $\beta_a$ ), and the current density ( $I_{\text{corr}}$ ), the values of the inhibition efficiency IE (%) are calculated by the following formula:

$$IE (\%) = \frac{I_{\text{corr}} - I_{\text{corr(i)}}}{I_{\text{corr}}} \times 100 \quad (1)$$

With  $I_{\text{corr(i)}}$  :is the corrosion current densities of mild steel in an acidic solution with inhibitor;  $I_{\text{corr}}$  : is the corrosion current densities of mild steel in an acidic solution without inhibitor. The data in Table 2 indicate that corrosion current densities are inversely proportional to inhibitor concentration, while inhibitory efficiency increases with increasing inhibitor concentration, reaching a maximum near 95% at a concentration of  $10^{-3}$  M compound **3**. This result is consistent with the results obtained by the weight loss method.



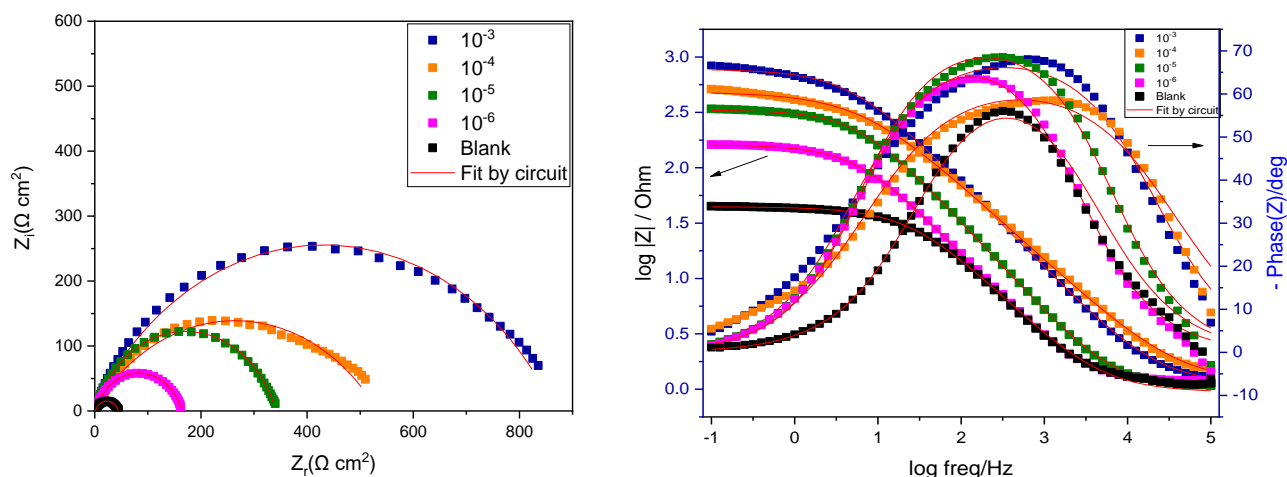
**Figure 2:** Polarization curves of mild steel in 1 M HCl without and with various concentrations of surfactant at 298 K.

**Table 2:** Tafel polarization parameters for mild steel in 1 M HCl medium without and with various concentrations of surfactants at 298 K.

Concentration (M)	$E_{\text{corr}}$ (mV/SCE)	$\beta_c$ (mV/dec)	$\beta_a$ (mV/dec)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	IE (%)
blank	-408.836	115	96.8	0.443	
$10^{-6}$	-377.985	75.6	64.3	0.118	73.36
$10^{-5}$	-375.935	88.1	66.3	0.054	87.81
$10^{-4}$	382.179	118.5	86.3	0.039	91.20
$10^{-3}$	-368.648	162.9	79.2	0.027	93.91

### 3.3. Electrochemical impedance spectroscopy (EIS)

The Nyquist and Bode electrochemical impedance spectroscopy (EIS) diagrams obtained for mild steel in 1M HCl medium in the absence and presence of surfactant **3** with different concentrations are shown in Figure 3. These measurements performed at a temperature of 298 K with an open circuit potential.



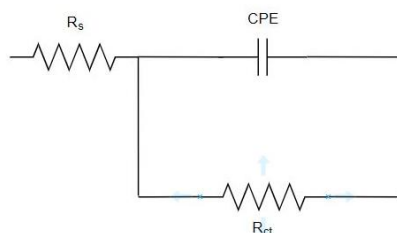
**Figure 3:** Nyquist and bode diagrams for mild steel in 1 M HCl without and with different concentrations of surfactant at 298 K.

From the spectroscopic impedance values in a corrosive medium with and without inhibitor, the percentage of corrosion inhibition can be determined. These measurements helped us to clarify some of the reaction mechanisms in the basic processes (adsorption, transfer, and charge diffusion) [38]. The plots are in the shape of a semicircle, which indicates that the process was primarily under the control of the capacitance, also the depressed semicircles have usually reflected the roughness and the inhomogeneity of electrode, like those identified in the event of adsorption process [39–41]. In addition, the values for the slope of the Bode-modulus plots ( $\log|Z|$  vs.  $\log f$ ) differ from -1 (Fig. 3), which are commonly found in solid electrodes due to the frequency dispersion of the interfacial impedance. At high frequencies, the semicircular loop shows the phenomenon resulting from the electrical double layer [4]. The addition of surfactant in different concentrations does not modify the shape of the depressed semicircle, but it increases their diameters, it increases with the increase in inhibitor concentration, which means that the addition of the inhibitor does not affect corrosion mechanism. The similar behavior is also observed on the Bode-modulus parcels. These data illustrate the adsorption of surfactant upon the metal surface. It inhibits corrosion by forming a protective film between the metal surface and the corrosive solution [40]. Table 3 shows the values of the double-layer capacitance, the load transfer resistance supplied by the Nyquist diagram, and the inhibition efficiency calculated from these data.

**Table 3:** Electrochemical impedance parameters of mild steel in 1 M HCl medium without and with various concentrations of surfactants at 298 K.

Concentration (M)	$R_s$ ( $\Omega \cdot \text{cm}^2$ )	CPE Q ( $\mu\text{F S}^{n-1}$ $\text{cm}^{-2}$ )	n	$R_p$ ( $\Omega \cdot \text{cm}^2$ )	Cdl ( $\mu\text{F} \cdot \text{cm}^{-2}$ )	$\tau$ (s)	IE (%)
blank	1.097	366.56	0.79647	42.93	126.88	0.00545	
$10^{-6}$	1.157	321.54	0.81113	160.6	161.27	0.02590	73.27
$10^{-5}$	1.029	147.93	0.8274	331.6	78.87	0.02615	87.05
$10^{-4}$	1.141	146.75	0.70408	484.6	48.31	0.02341	91.14
$10^{-3}$	1.111	88.25	0.77949	783.1	41.44	0.03245	94.52

From the impedance data (Table 5), we can notice the value of  $R_p$  increases with the increase of inhibitor concentration, which indicates that the highest corrosion efficiency reaches the maximum value of 94.52% at a concentration of  $10^{-3}$  M. However, when the concentration shifts to the minimum value, the double-layer capacitance decreases, which indicates that the inhibitor studied has adsorbed. The results obtained led us to recommend forming a protective film on the electrode surface.

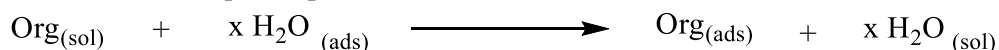


**Figure 4:** The equivalent electrical circuit model used in the experimental impedance fit.

The equivalent circuit shown in figure 5 was used to obtain the best fit of the graph. The proposed circuit has a solution resistance ( $R_s$ ), a charge transfer resistance ( $R_{ct}$ ) and a constant phase element (CPE). Usually, the CPE element is used to explain the recess in the semicircle of the capacitor. Such depressions usually indicate surface metal heterogeneity due to roughness, impurities and the formation of porous layers.

### 3.4. Adsorption isotherm

The adsorption isotherm studies are carried out to clarify the mechanism involved in corrosion inhibition; they explain the molecular interactions between active sites on the surface of mild steel and molecular inhibitors [42]. Considering that, in the absence of the inhibitor, the adsorption of water molecules contained in the solvent to the metal surface takes place primarily. Thus, in the presence of the inhibitor, the adsorption of the inhibitor molecules may be considered as a quasi-substitution between the water molecules adsorbed on the metal surface and the inhibitor molecules in the aqueous phase [43].



Where  $x$  is the ratio of the size factors corresponding to the number of water molecules that are replaced by an organic inhibitor molecule. It is presumed to be independent of electrode coverage or charge [44]. The surface coverage ( $\theta$ ), which is the area of the metal surface coated with inhibitor molecules, indicates that a molecular layer is formed between the metal surface and the corrosive environment. Inhibitor molecules can be adsorbed on the metal surface by the formation of covalent or electrostatic bonds between the metal atoms and the adsorbates [45]. In this study, we have examined several adsorption isotherms such as Langmuir, Frumkin, and Temkin in order to have an isotherm that describes the best adsorption process. Based on these isotherms, the surface coverage ( $\theta$ ) is directly related to the inhibitor concentration ( $C_{inh}$ ) according to these equations:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (\text{Langmuir isotherm}) \quad (2)$$

$$\left(\frac{\theta}{1-\theta}\right) \exp(2\alpha\theta) = K_{ads} C_{inh} \quad (\text{Frumkin isotherm}) \quad (3)$$

$$\exp(-2\alpha\theta) = K_{ads} C_{inh} \quad (\text{Temkin isotherm}) \quad (4)$$

Where  $\theta$  is the surface coverage;  $C_{inh}$  is the surfactant concentration;  $K_{ads}$  is the adsorption equilibrium constant and  $\alpha$  is the molecular interaction constant; the values of  $\theta$  for various concentrations of surfactant at 298 K, shown in Table 1, are readily obtained from, potentiodynamic polarization tests ( $\theta_{pp}$ ), electrochemical impedance spectroscopy ( $\theta_{EIS}$ )



and mass loss methods ( $\theta_{ML}$ ). If we assume that, the values of IE % are not significantly different from those of  $\theta$ , in each case the values of  $\theta$  are calculated by the ratio IE % according to the following equations (5), (6) and (7):

$$\theta_{PP} = 1 - \left( \frac{I_{corr(i)}}{I_{corr}} \right) = IE\% / 100 \quad (5)$$

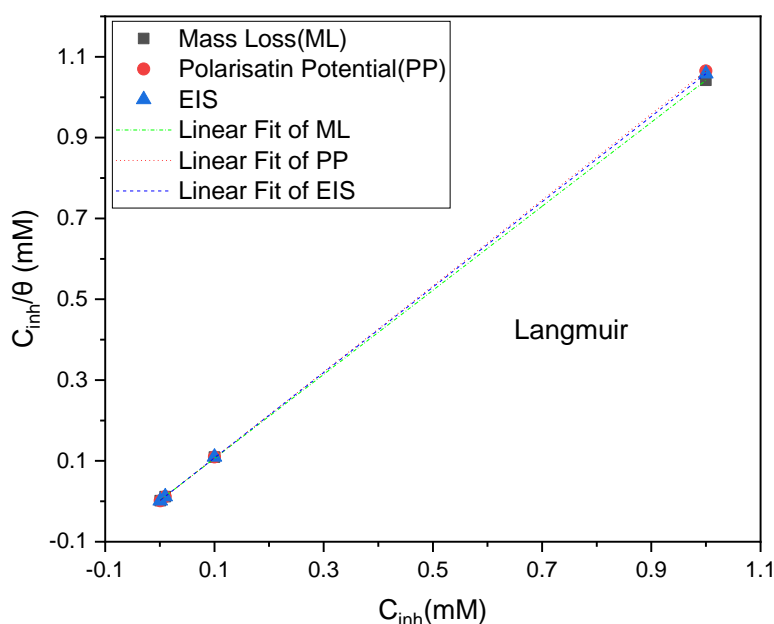
$$\theta_{EIS} = 1 - \frac{R_{Ct}}{R_{Ct,inh}} = IE\% / 100 \quad (6)$$

$$\theta_{ML} = 1 - \frac{W_{corr}}{W_{corr,inh}} = IE\% / 100 \quad (7)$$

The surface coverage values obtained by different methods; potentiodynamic polarization ( $\theta_{PP}$ ), electrochemical impedance spectroscopy ( $\theta_{EIS}$ ), and mass loss ( $\theta_{ML}$ ) for mild steel in 1 M HCl at a range concentration of surfactant at 298 K are illustrated in the table 4.

**Table 4:** Surface coverage obtained by the three methods studied

$C_{inh} \text{ (mol.L}^{-1}\text{)}$	$\theta_{PP}$	$\theta_{EIS}$	$\theta_{ML}$
$10^{-6}$	0.734	0.733	0.688
$10^{-5}$	0.878	0.871	0.879
$10^{-4}$	0.912	0.911	0.913
$10^{-3}$	0.939	0.945	0.959



**Figure 5:** Langmuir's isotherm adsorption plot of the surfactant on the surface of mild steel in 1 M HCl at 298 K.

To determine the most appropriate isotherm for this study, the  $R^2$  correlation coefficient was used and the Langmuir isotherm presents the best fit (Fig.5); for which the  $R^2$  value is very close to one. This indicates that the adsorption of surfactant molecules on the surface of the mild steel in a 1 M HCl solution follows the Langmuir adsorption model. Langmuir adsorption isotherm assumes that the surface of the metal is homogeneous so that the number of sites on the adsorption surface is fixed, furthermore, all sites are identical and each site can only absorb one species. Also, the Langmuir model suggests that there are no lateral interactions between the molecules adsorbed on the metal surface[46]. The free energy of adsorption of Gibbs standard,  $\Delta G_{ads}$  linked to the adsorption constant  $K_{ads}$  through the relation:



$$K_{ads} = \frac{1}{55.55} \exp\left(\frac{-\Delta G_{ads}^{\circ}}{RT}\right) \quad (8)$$

Where T is the temperature in Kelvin, R is the universal gas constant; its value is  $R = 8.314 \text{ J.Mol}^{-1}.\text{K}^{-1}$ , the value 55.55 in the above equation is the concentration of  $\text{H}_2\text{O}$  in solution in  $\text{Mol.l}^{-1}$ , and  $K_{ads}$  obtained from the interception of the  $C_{inh}/\theta$  line.

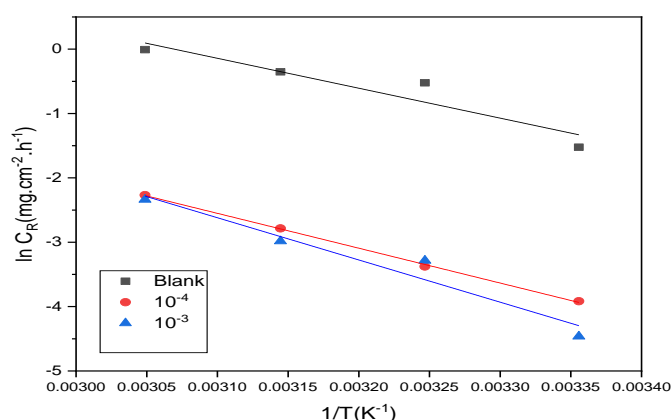
**Table 5:** Adsorption parameters obtained from the linearization of the adsorption isotherm for corrosion of mild steel in 1.0 M HCl in the presence of surfactant at 298 K.

Method	R <sup>2</sup>	Slope	K <sub>ads</sub> (L mol <sup>-1</sup> )	ΔG <sub>ads</sub> (kJ mol <sup>-1</sup> )
Mass Loss	0.9999	1.039	4.5 10 <sup>5</sup>	-32.28
EIS	0.9999	1.056	5.9 10 <sup>5</sup>	-32.92
Potentiodynamic Polarization	0.9999	1.063	7.2 10 <sup>5</sup>	-33.42

The values for  $K_{ads}$  and  $\Delta G_{ads}$  are shown in Table 5; the negative value of  $\Delta G_{ads}$  indicates that the adsorption process is spontaneous and the adsorbed film on the steel surface is stabilized [47]. Literature shows that  $\Delta G_{ads}$  values less than or equal to 20 KJ .mol<sup>-1</sup> correspond to Physisorption, those greater than or equal to 40 kj.mol<sup>-1</sup> Adsorption refers to the chemisorption process, i.e. a transfer or sharing of charges on the metal surface [11]. In this study, values obtained from  $\Delta G_{ads}$  ranged from -20 kJ mol<sup>-1</sup> to -40 kJ mol<sup>-1</sup>, which suggests that the inhibitor adsorbs by both physisorption and chemisorption; it is a mixed type inhibitor [5].

### 3.5. Temperature effects

The inhibitory activity of the surfactant was tested at different temperatures based on weight measurements. The results illustrated in figure 6 show that the increase in temperature significantly increases the CR, which is probably due to the desorption of the surfactant molecules adsorbed on the surface of the mild steel at high temperatures [33]. On the other hand, the inhibitory efficacy of the inhibitor decreases with increasing temperature. This result suggests the physical adsorption of surfactant molecules on the surface of mild steel [25].



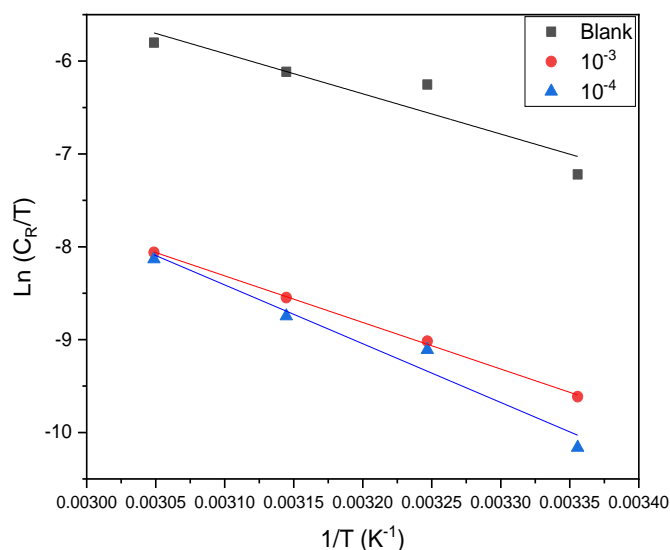
**Figure 6:** Arrhenius plots for the corrosion rate of mild steel in 1 M HCl with optimized concentrations of surfactant. The Arrhenius equation has been used to determine the thermodynamic parameters of corrosion to understand the effect of temperature on the corrosion process.

$$C_R = A \exp(-Ea/RT) \quad (9)$$

Where  $C_R$  represents the corrosion rate,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the perfect gas constant and  $T$  is the absolute temperature. In the literature, it is proposed that the positive shift in activation energy values in the presence of an inhibitor is consistent with the physical adsorption process, whereas the Chemisorption is referred when the shift in activation energy values is negative [48]. The activation energy in the presence of the inhibitor is higher than that of the blank, and the  $E_a$  value of the blank solution is 38.6 kJ/mol is lower than in the presence of surfactant, indicating that the surfactant is adsorbed on the metal surface by physisorption. It is generally transmitted by the formation of an adsorption film through an electrostatic physical process.

**Table 6:** Activation parameters for mild steel in 1.0 M HCl in the presence and the absence of surfactant at 298 K.

Concentration (M)	$E_a$ (kJ/mol)	$\Delta H_a$ (kJ/mol)	$\Delta S_a$ (J/mol/K)
Blank	38.64991	36.05232	-134.985
$10^{-4}$	45.01491	41.72045	-137.32
$10^{-3}$	54.53532	52.6346	-104.298



**Figure 4:** Plots of  $\ln (C_R/T)$  vs  $1/T$  for mild steel in 1 M HCl with optimized concentrations of surfactant.

Besides, the values of the activation entropy ( $\Delta S_a$ ) and the activation enthalpy ( $\Delta H_a$ ) were calculated from the alternative formula of the Arrhenius equation.

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta H_a}{R}\right) \exp\left(\frac{-\Delta S_a}{RT}\right) \quad (10)$$

Where,  $h$  is Plank's constant,  $N$  is Avogadro's constant.

The values for ( $\Delta H_a$ ) and ( $\Delta S_a$ ) are given in Table 5. It is observed that the values for  $\Delta H_a$  are higher in the presence of the inhibitor compared to the control solution. The positive value of  $\Delta H_a$  suggests that the corrosion process of steel in acid solution is endothermic and that in the presence of the surfactant, this process is reduced [49,50]. Thus,  $\Delta S_a$  values increase positively in the presence of the surfactant compared to the control solution. This means that water molecules are repelled by the surfactant molecules on the surface of the metal, which increases the disorder of the corrosion system [51,52].

## 4. Conclusion

In the present study, the surfactant derived from isatin is synthesized and assessed as an anti-corrosion agent for steel in an acidic environment. The compound was chosen for its ease of synthesis and its multiple coordination sites for mild steel, in the form of a pair of isolated electrons on oxygen and nitrogen as well as  $\pi$ -electrons on the aromatic ring. The compound has shown excellent inhibition efficiency and that its inhibition properties increase with increasing concentration. It functions as a mixed type inhibitor with anodic predominance in a solution of hydrochloric acid for mild steel. The process of corrosion of mild steel is retarded by the adsorption of surfactant on the metallic surface and obeys the Langmuir isotherm. The relative value of  $\Delta G^{\circ}_{\text{ads}}$  revealed that the adsorption mechanism of the surfactant derived from isatin is mixed (both chemisorption and physisorption).

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