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Study of new 5-Chloro-Isatin derivatives as efficient organic inhibitors of corrosion in 1M HCl medium: Electrochemical and SEM studies

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Abstract
The effect of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione as a corrosion inhibitor on mild steel in 1M HCl solution was studied through weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Scanning electron microscopy (SEM) was employed to analyze the surface topography of the uninhibited and inhibited mild steel. The inhibition efficiency of the inhibiting compound increases with increase in inhibitor concentration at 303K, resulting in significant decrease in corrosion rate of the mild steel. Thermodynamic adsorption and activation parameters were calculated for the corrosion inhibition process adsorption of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione on the steel obeyed the Langmuir adsorption model.

Keywords: Corrosion, mild steel, 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione, HCl, inhibition, EIS

1. Introduction
The use of inhibitors is one of the most practical methods to protect steel against corrosion in acidic solutions [1]. The majority of inhibitors used in the industry are organic compounds mainly consisting of nitrogen, oxygen and sulfur, as well as inhibitors that contain double or triple bonds facilitate the adsorption of these compounds on the metal surfaces [2].
The study of corrosion processes and organic inhibitions is a very interesting area of research [3,4]. Many scientists have reported that the mechanism of inhibition is mostly explained by certain physicochemical and electronic properties of the organic inhibitor that relate to steric effects, its functional groups, the orbital nature of donating electrons, and the electron density of the donor atoms and so on [5,6]. The use of organic inhibitors such as 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione are also studied for their usefulness in various industries to control the corrosion of metals [7, 8].

The chemistry of these heterocyclic compounds play an active role in the development of new pharmaceutical materials new properties, the study of their various biological activities including its application in the field of agriculture and the pharmaceutical industry, they are used as anti-tumor [9], antibacterial, antifungal, antiviral antiphrastic, anti-tubercular agents, insecticides and some of these compounds also have anti-inflammatory, anti-diabetics [10-13], and anesthetics [14] properties. The aim of this study is to evaluate the corrosion inhibition of mild steel in 1M hydrochloric acid (HCl) with 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione synthesized [15-17] and showed in Figure 1.

2. Materials and methods

2.1. Synthesis of the inhibiting compound

The synthesis of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione is given by the reaction of 5-chloro-1*H*-indole-2,3-dione with the alkylating agent Bromo-*N*,*N*-dimethylethanamine using DMF as solvent[18], under conditions of catalysis by phase transfer in the presence of a base K_2CO_3 and a TBAB catalyst at a room temperature, gives a good yield, the reaction is diagrammed below (Figure 1).Then the mixture evaporated under reduced pressure, the residue treated reaction and the product is purified on a silica gel column (eluent (ethyl acetate / hexane)).

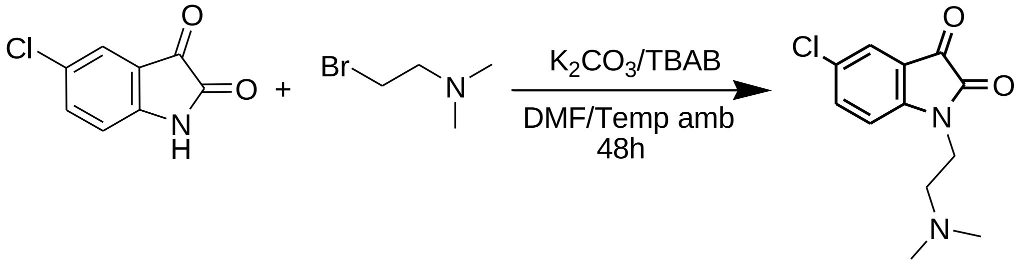

Figure 1: Synthesis of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione

The analytical data of the nuclear magnetic resonance NMR spectra and Infrared spectroscopy were consistent with the structure of the compound formed.

Yield(%)=89% ; F(°C)= 114 ; NMR ^1H ($CDCl_3$)δppm 7.53-7.54(m, H, H_{Ar}) ; 7.51(d, H, H_{Ar}, J=9Hz); 6.90(d, H, H_{Ar}, J=9Hz); 3.85(t, 2H, CH_2, J=9Hz); 3.75(t, 2H, CH_2, J=9Hz); 2.15(m, 6H, CH_3).NMR^{13}C($CDCl_3$)δppm : 184.59(C=O) ; 164.45(N-C=O) ; 146.22, 141.13, 110.39(Cq) ; 138.59, 126.08, 113.36(CH_{Ar}) ; 55.90,46.79(CH_2) ; 45.09(CH_3).Infra Red υ_{max} (KBr)/cm^{-1}: 3565, 3174, 3081, 2975, 1720, 1607, 1445, 1123, 701, 461.

2.2. material

The steel used in this study is a mild steel having a composition of 0.370% C, 0.230% Mn 0.680% Si, 0.016% S, 0.077% Cr , 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% of Cu and the balance being iron (Fe), shape and surface of dimensions 1.5 x 1.5 cm. Before performing experiments by grinding, the samples were pretreated with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone, washed again with bidistilled water and then dried at room temperature before use.

2.3. Solutions

Solutions 1 M HCl test were prepared by dilution of reagent grade HCl 37% with distilled water. The 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione was dissolved in an acidic solution at a range of concentrations and the required solution in the absence of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione was taken as empty to make the comparison in the future.

2.4. Corrosion tests

In order to determine the characteristics of corrosion inhibitors of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione in 1 M HCl medium, we chose to work on three conventional techniques [19].

The weight loss measurements, electrochemical impedance spectroscopy of (EIS) and potentiodynamic polarization curves [20].

The gravimetric tests were developed on rectangular test specimens of size (1.5 cm x 1.5 cm x 0.3 cm) in a 1M HCl solution[21], The immersion time was 6 hours at room temperature (30 ±1°C) with and without the addition of different concentrations of 5-chloro-1-(2- (dimethylamino) ethyl) indoline-2,3-dione.

Using an analytical balance (accuracy ± 0.1 mg). The weight of each sample was measured before and after the test with accuracy, the samples were immersed in the solutions, and at the end of the test, they were collected, carefully washed and weighed [22,23]. The experiments were made in triplicate for each case after exposure to

1 M HCl solution with and without addition of various concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione.

2.5. Electrochemical measurements

The electrochemical measurements were performed using a potentiostat PGZ100 VoltaMaster controlled by software. The potentiodynamic polarization measurements were made in a cylindrical corrosion cell in conventional three Pyrex glass electrodes.

The temperature is thermostatically controlled at 30 ± 1 °C the mild steel sample was used as working electrode, a platinum electrode as against electrode and a saturated calomel electrode (SCE) as the reference electrode, the surface exposed to the electrolyte of 1 cm².

The electrochemical impedance spectroscopy (EIS) measurements are made with the electrochemical system (Tacussel), which included a model of digital potentiostat computer VoltaLab PGZ100 to E_{corr} after immersion in solution without bubbles. After measuring the current at steady state to a corrosion potential, sinusoidal voltage (10 mV) peak-to-peak at frequencies between 100 kHz and 10 MHz is superimposed on the resting potential.

Measurements at resting potential after immersion at 303 K were controlled automatically by computer programs, the impedance diagrams are given in the Nyquist representation, and to ensure reproducibility we repeated the experiments three times.

2.6. SEM study

The morphologies of the uninhibited and inhibited mild steel surface were analyzed by scanning electron microscope (FEI Quanta 200) equipped with EDAX probe for microanalysis of surfaces. The acceleration voltage employed was 0.5 to 30 kV with a resolution of 3.5nm.

3. Results and discussion

3.1. Weight Loss study

The weight loss method was applied to investigate the effect of the addition of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione as tested at different concentrations on the corrosion of the mild steel in 1 M HCl solution at 303 K, after 6 hours of immersion period. Data from this study such as gravimetric weight loss, corrosion rates, efficiency and the surface coverage were calculated according to equations (1),(2) and (3) respectively [24,25]:

$$C_R = \frac{W_b - W_a}{At} \quad (1)$$

$$\eta_{WL}(\%) = \left(1 - \frac{w_i}{w_0}\right) \times 100 \quad (2)$$

$$\theta = \left(1 - \frac{w_i}{w_0}\right) \quad (3)$$

With W_a and W_b are the specimen weight before and after immersion in 1M HCl, A is a sample surface of mild steel (cm^2), t is the exposure time (h),w_0 and w_i are the values of losses weight of corrosion of mild steel in uninhibited and inhibited solutions.

The values obtained for the corrosion rate (C_R) and the efficiency (η%) were summarized in Table 1,the variation of the inhibition efficiency(%) and corrosion rate versus concentrations of the 5-chloro-1-(2(dimethylamino) ethyl) indoline-2,3-dione are shown in Figure 2. it is clear that from these results that the 5-chloro-1-(2(dimethylamino) ethyl) indoline-2,3-dione inhibits the corrosion of mild steel in all the concentrations used, it may be observed that the (C_R) of mild steel decreases so that the efficiency of the protection increases with increasing of the concentration of additive in 1M solution of HCl at 303K.

Table 1: The efficiency and the corrosion rate in the presence and absence of different concentrations of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione in 1M HCl

Concentration (M)	C_R ($mg.cm^{-2}.h^{-1}$)	η (%)	θ
HCl 1M	0.451	--	--
10^{-3}	0.038	91.57	0.915
5.10^{-4}	0.067	85.14	0.851
10^{-4}	0.075	83.37	0.833
5.10^{-5}	0.144	68.07	0.680
10^{-5}	0.218	51.66	0.516
10^{-6}	0.242	46.34	0.463

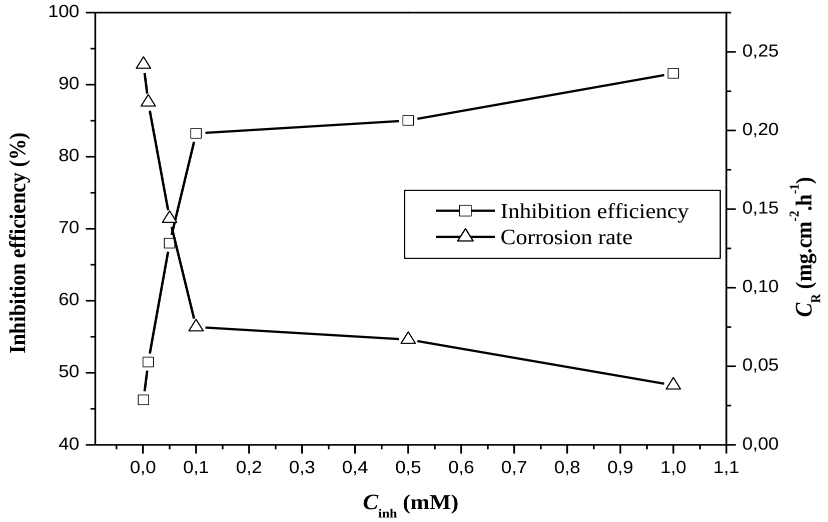

Figure2: Variation of inhibition efficiency and corrosion rate of mild steel in various concentrations of 1 M HCl in the product

3.2. Potentiodynamic measurements:
3.2.1. Tafel polarisation study

Figure 3 shows the curves Tafel in solutions of 1 M HCl with and without the addition of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione at various concentrations.

The values of the electrochemical parameters obtained from the Tafel curves are: the corrosion potential (E_{corr}), cathodic Tafel slope, anodic Tafel slope, corrosion current density (I_{corr}), inhibition efficiency E_I(%) for different concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione are shown in Table 2.

The inhibition efficiency E_I was calculated from the transfer of the resistance values of load using the following equation [26]:

$$E_I\% = \frac{I_{corr} - I_{corr\ (inh)}}{I_{corr}} \times 100 \quad (4)$$

With I_{corr} and $I_{corr(inh)}$ are the values of corrosion current densities steel in the absence and presence of the additive, respectively, which were obtained by cathodic Tafel extrapolation lines to the corrosion potential E_{corr}.

Figure 3 shows the potentiodynamic polarization curves of mild steel 1M HCl in the absence and the presence of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione these potentiodynamic polarization curves illustrate that the presence of our product caused a decrease in both the anodic tafel and cathodic slope, with a decrease more pronounced in the cathodic branch, demonstrating that this product acts as a mixed inhibitor Type with essentially cathodic characteristics.

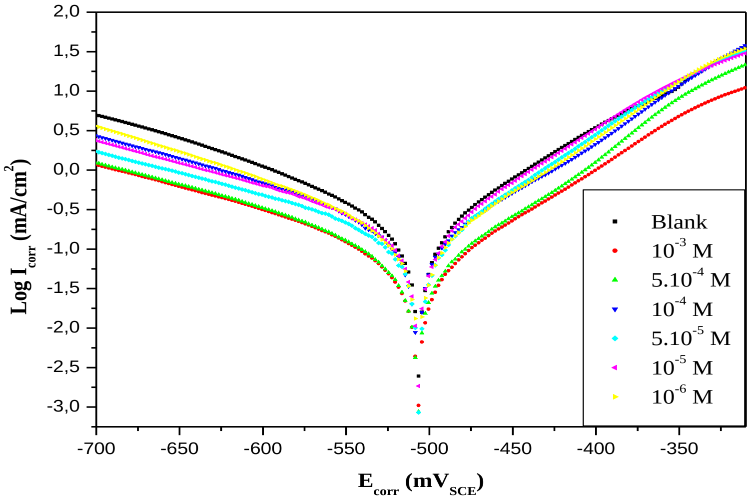

Figure 3: Curves of mild steel potentiodynamic polarization at various concentration of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione in a solution of hydrochloric acid 1M.

Table 2: Potentiodynamic polarization parameters at different concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione in 1M HCl.

	Conc (M)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} (µA/cm²)	E_I (%)
Blank	1	506.5	172.4	3818	--
Product	10^{-6}	503.4	174.4	2114	44.63
	10^{-5}	499.9	175.7	1885	50.62
	5.10^{-5}	493.6	179.1	1429	62.57
	10^{-4}	498.1	186.4	1138	70.19
	5.10^{-4}	496.4	187.4	1090	71.45
	10^{-3}	483.4	197.7	761	80.06

These results can be explained by the adsorption of organic compounds present in the solution of 1M HCl at the active sites of the electrode surface. While Table 2 shows that the corrosion current density (I_{corr}) decreased in the presence of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione.

3.2.2. Ac impedance study

Nyquist plot of mild steel in1M HCl in the presence and the absence of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione was studied by (EIS) at 308K and presented in Figure 4. After analyzing the form of Nyquist plots, it was concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was essentially controlled by the charge transfer [27]. The general shape of the curves is very similar for all samples; it is maintained throughout the concentration, indicating that almost no change in the corrosion mechanism by the addition of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione [28]. Based on the equations (5) and (6) is determined successively inhibition efficiency using charge transfer resistance while the double-layer capacity (C_{dl}):

$$\eta\% = \frac{R_{ct\,(in\,h)} - R_{ct}}{R_{ct\,(in\,h)}} \times 100 \qquad (5)$$

$$C_{dl} = (A\,R_{ct}^{1-n})^{1/n} \qquad (6)$$

The impedance parameter such as charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}), and efficiency of inhibition are shown in Tables 3.

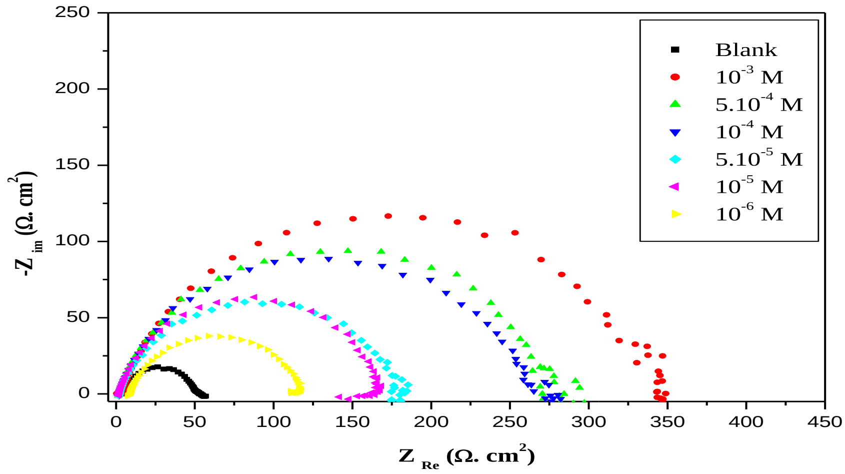

Figure 4: Impedance plot of mild steel obtained in the absence and presence of various concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione in 1M HCl.

Table 3: Settings improved features from the steel impedance diagram in 1M HCl to various concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione**.**

	Con (M)	R_t (Ω. cm²)	R_{ct} (Ω. cm²)	N	C_{dl} (µF/cm²)	η (%)
Blank	1	4.88	48	0.91	66.30	--
Product	10^{-6}	2.39	118.3	0.97	68.56	59.42
	10^{-5}	2.67	154.1	0.89	62.45	68.85
	5.10^{-5}	1.92	177.4	0.95	71.75	72.94
	10^{-4}	1.08	269.3	0.97	59.08	82.17
	5.10^{-4}	1.27	279.8	0.93	56.88	82.84
	10^{-3}	2.92	342.8	0.98	46.42	85.99

It was clear that the values of R_{ct} charge transfer resistance has been increased and the capacity C_{dl} values decreased with increasing concentration of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione increased R_{ct} charge transfer resistance is associated with a system slower corrosion.

Improving the corrosion resistance of mild steel in acid medium results in an increase in charge transfer resistance values could be attributed to adsorption of the inhibitor to the acid-steel interface, which effectively blocked the active sites on the surface of the mild steel and therefore the reduction of C_{dl} values with an increase in the concentration of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione, suggesting that the thickness of the protective layer increases with decreasing the constant local dielectric [29].Increasing the efficiency of inhibition with increased concentration of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione promotes increasingly cover the surface of the mild steel with the inhibitor concentrations.

3.3. Effect of temperature

3.3.1. Corrosion kinetic study

In order to evaluate the effect of temperature on the efficiency of inhibition of 5-chloro-1(2-(dimethylamino) ethyl) indoline-2,3-dione several experiments were studied by the method of weight loss in the temperature ranges from 303 to 333 K, the values of the corrosion rate in the absence and the presence of the optimal concentration of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione at different temperatures are given in the Table 4. The corrosion rates obtained increases with increasing temperature for the two acid solutions inhibited and not inhibited while they decreased with increasing inhibitor concentration for all temperatures.

Table 4: The corrosion parameters of mild steel in 1M HCl acid in the absence and presence of the optimal concentration of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione at different temperatures studied 1h

Température	C_{inh} (mol/L)	C_R (mg.cm^{-2}.h^{-1})	η (%)	θ
303	Blank	0.080	---	---
	10^{-3}	0.005	93.7	0.937
	10^{-4}	0.019	76.2	0.762
	10^{-5}	0.037	53.7	0.537
	10^{-6}	0.054	32.5	0.325
313	Blank	0.101	---	---
	10^{-3}	0.008	92.0	0.920
	10^{-4}	0.030	70.2	0.702
	10^{-5}	0.054	46.5	0.465
	10^{-6}	0.073	27.7	0.277
323	Blank	0.388	---	---
	10^{-3}	0.041	89.4	0.894
	10^{-4}	0.153	60.5	0.605
	10^{-5}	0.254	34.5	0.345
	10^{-6}	0.316	18.5	0.185
333	Blank	0.615	---	---
	10^{-3}	0.124	79.8	0.798
	10^{-4}	0.285	53.6	0.536
	10^{-5}	0.426	30.7	0.307
	10^{-6}	0.550	10.5	0.105

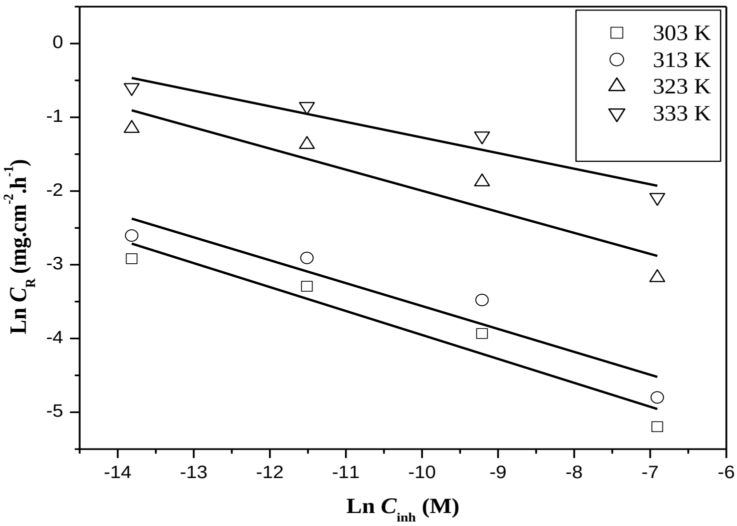

Figure 5: Variation of LnC_R with LnC_{inh} for mild steel of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione at various temperatures in1M HCl

The data in Table 4 show that the addition of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione results in a reduction of the corrosion rate of mild steel in 1 M HCl. .While the inhibition efficiency (η) increases with increasing inhibitor concentration at all temperatures, at a concentration of 10^{-3}M it's seen that the inhibition efficiency is maximum. This may explain why inhibitory molecules act by adsorption on the metal surface [30], to understand the mechanism of inhibition, it was determined by the thermodynamic functions for the dissolution of mild steel with and without the addition of the optimal concentration of 5-chloro-1-(2-

(dimethylamino)ethyl) indoline-2,3-dione at varying temperatures, which have been calculated from the logarithm of the corrosion rate (C_R) of metal in 1M HCl acid solution using the kinetic equation [31,32] :

$LnC_R = BLnC_{inh} + Lnk$ (7)

Where C_R is the corrosion rate, k is the rate constant, B is the constant of reaction in this case is a measure of the inhibition efficiency, and C_{inh} is the concentration of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione.

Table 5: The kinetic parameters of the corrosion of mild steel at different temperatures in1 M HCl

Temperature (K)	*B*	*k* (mg.cm^{-2}.h^{-1})
303	-0.324	0.0007
313	-0.310	0.001
323	-0.285	0.007
333	-0.211	0.033

The activation thermodynamic parameters for the corrosion process were calculated from the equation of Arrhenius. The formulation and replacement of the transition state equation is shown in Eq. (8) and (9):

$$C_R = Aexp\left(-\frac{E_a}{RT}\right) \quad (8)$$

$$C_R = \frac{RT}{Nh}\, exp\left(\frac{\Delta S_a}{R}\right)\, exp\left(-\frac{\Delta H_a}{RT}\right) \quad (9)$$

Where, E_a is the apparent activation energy of the corrosion, R is the universal gas constant, T is the absolute temperature, and A is the pre-exponential constant Arrhenius. h is Plank's constant, N is the number of Avogadro constant Planck ΔS_a is the entropy of activation and ΔH_a is enthalpy of the activation.

This equation can be represented graphically by plotting the natural logarithm of the corrosion rates versus 1/T with and without addition of various concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione in 1M HCl shown in Table 6.

Table 6: Thermodynamic parameters Kinetic corrosion of mild steel in 1M HCl in the absence and the presence of various concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione.

C_{inh} (mol/L)	E_a (kJ.mol^{-1})	ΔH_a (kJ.mol^{-1})	ΔS_a (J.mol^{-1}.K^{-1})	E_a-ΔH_a
Blank	62.17	59.53	-70.88	2.639
10^{-6}	70.41	67.77	-47.07	2.639
10^{-5}	74.17	71.54	-37.63	2.639
10^{-4}	80.73	77.84	-21.40	2.889
10^{-3}	91.46	88.83	2.58	2.635

The plots obtained are straight lines and the activation energy was estimated from the slope of straight lines of plots, plots are shown in Figure 6. From the Table 6 we can see that the values of E_a are higher in the presence of the 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione from its absence in a solution of HCl, it indicates that the inhibitor induces the energy barrier for the corrosion reaction which leads to the decrease of the corrosion rate of mild steel in the presence of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione [33-34].The figure 7 shows a log graph (C_R/T) against (1000/T). Straight lines are obtained with a slope of ($-\Delta H_a$/R) and an intercept (log $R/Nh+\Delta S_a/R$) from which values ΔH_a and ΔS_a are calculated and reported in the Table 6.

In the presence of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione, we see that the values of ΔH_a are higher (67.77 to 88.83 kJ.mol^{-1}), which reflects the endothermic nature of the process of dissolution of mild steel, we find that values of E_a and ΔH_a changes in the same way, which allows us to verify the equation between thermodynamics and E_a, ΔH_a.

$\Delta H_a = E_a - RT$ (10)

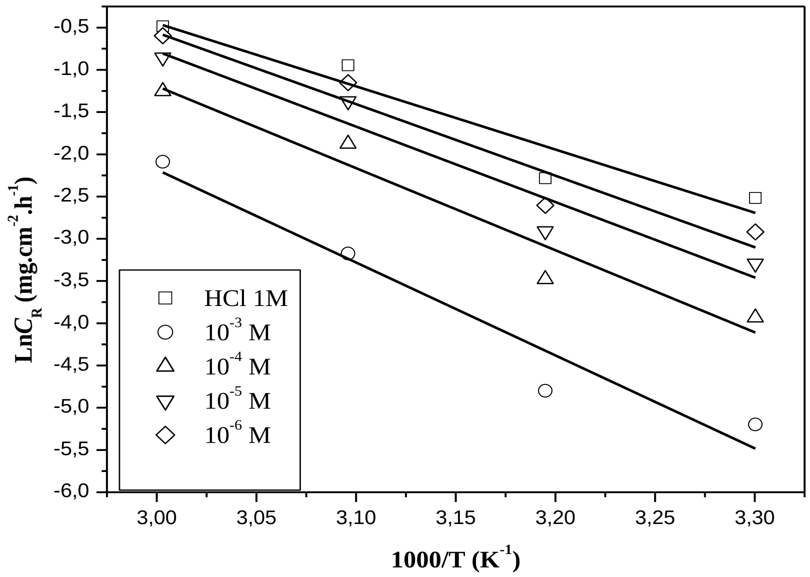

Figure 6: Arrhenius plots of mild steel corrosion rate (C_R) in 1M HCl corresponding to the studied of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione

From the table 6 we can see that the value of entropy (ΔS_a) increase with increasing concentrations implying that the complex activated tariffs determination step represents an association rather than splitting it which means that the disorder of decreased inhibitory molecules on the surface of the mild steel, instead of going from reactants to the activated complex [35,36].

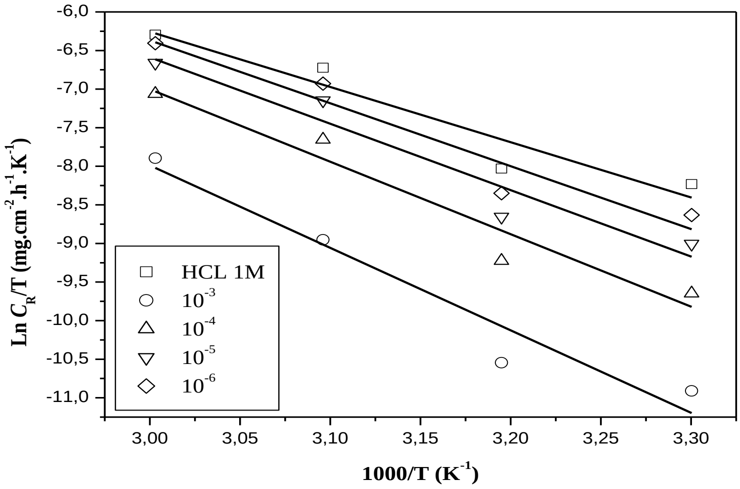

Figure 7: Plots corrosion rate of transition state (C_R) mild steel in 1M HCl in the absence and presence of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione.

3.3.2. Adsorption isotherm and thermodynamic parameters

The adsorption isotherms are considered to describe the interactions between the inhibitor molecule with the active sites on mild steel, The efficiency of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dioneas a successful corrosion inhibitor depends mainly on its adsorption capacity on the metal surface [37]. However, the best fit was obtained from the Langmuir isotherm (Figure 8). This model assumes that the solid surface contains a fixed number of adsorption sites [38, 39].

The isotherm calculated and plotted the data points are in Figure8. A good fit is observed with the regression coefficients up to 0.9, which implies that the experimental data are well described by Langmuir isotherm [40].

$$Ln\frac{\theta}{1-\theta} = LnK + yLnC_{inh} \qquad (11)$$

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (12)$$

Where θ is the surface coverage degree, C is the inhibitor concentration in the electrolyte and K is the equilibrium constant of the adsorption process.

The Langmuir isotherm cannot be strictly applied because of the deflection unit of the slope (1,226 at T°= 333 K), this is why, the experimental data were fitted to the kinetic model/thermodynamics El-Awady (Figure 9) [41]. The constant of adsorption, K_{ads}, is related to the standard free energy of adsorption $\Delta G°_{ads}$, with the following equation:

$$K_{ads} = \frac{1}{C_{H_2O}} exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (13)$$

Where R is the universal gas constant, T the thermodynamic temperature and the concentration of water in the solution is 1000 g/l.

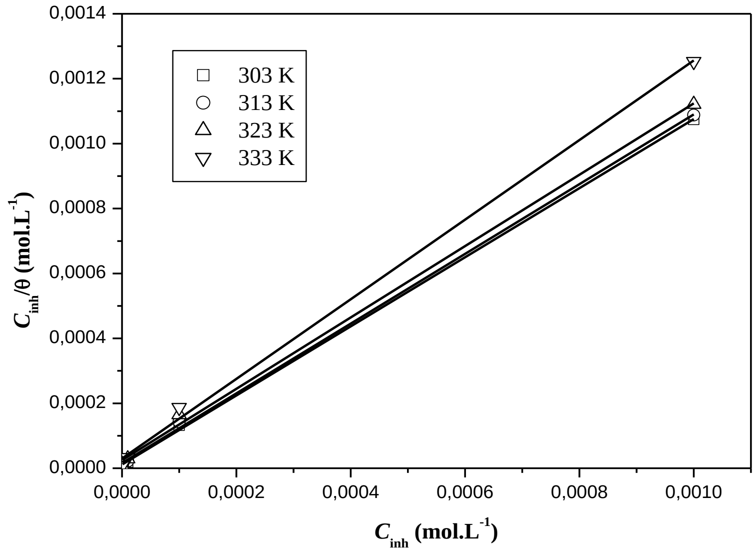

Figure 8: Langmuir adsorption isotherm of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione on mild steel in 1M HCl

Table 7: Adsorption of the inhibitor parameters studied in1M HCl obtained from Langmuir adsorption isotherm at different temperature

T (K)	R^2	Slope
303	0.9996	1.0641
313	0.9992	1.0743
323	0.9983	1.0991
333	0.9983	1.2266

The calculated parameters are reported in the Table 8. Negative values of the $\Delta G°_{ads}$ reflect spontaneous adsorption and strong interaction of inhibitory molecules on the surface of the mild steel. In general, values of $\Delta G°_{ads}$ around or below -20 $kJ.mol^{-1}$ are compatible with physisorption and those around or more negative than -40 $kJ.mol^{-1}$ involve chemisorptions [42].

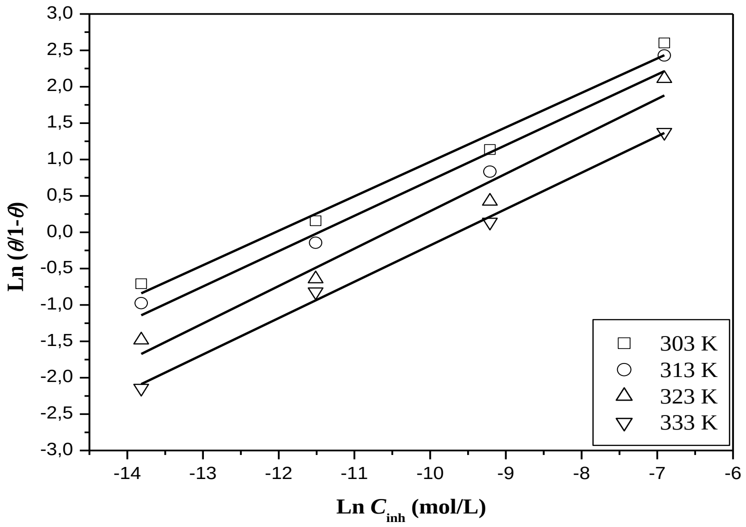

Figure 9: El-Awady's isotherm adsorption model at different temperatures

Table 8: Thermodynamic parameters for the adsorption of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione on the mild steel in 1 M HCl at different temperatures

T (K)	K_{ads} (mol/L)	R^2	$\Delta G°_{ads}$ (kJ.mol^{-1})
303	169546.2	0.9839	-40.45
313	90986.64	0.9754	-40.17
323	38008.58	0.9743	-39.11
333	15279.43	0.9966	-37.79

The calculated values for $\Delta G°_{ads}$ have been found in the range of -37.79 to -40.45 kJ.mol^{-1},at different temperatures (303-333 K), these values fall between the threshold values for the chemical adsorption. The equation (14) implies the relationship between $\Delta G°_{ads}$, $\Delta S°_{ads}$ and $\Delta H°_{ads}$.

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\,\Delta S^{\circ}_{ads} \quad (14)$$

A plot of $\Delta G°_{ads}$ vs. T gives straight lines (Figure 10) with the slope equal to - $\Delta S°_{ads}$, and the value of $\Delta H°_{ads}$ can be calculated from intercept (Table 9).

Table 9: Thermodynamic parameters for the adsorption of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione on mild steel in a1M HCl solution at different temperatures

T (K)	$\Delta H°_{ads}$ (KJ.mol^{-1})	$\Delta S°_{ads}$ (J.mol^{-1}.K^{-1})	$\Delta H°_{ads}$ (KJ.mol^{-1})	$\Delta S°_{ads}$ (J.mol^{-1}.K^{-1})	$\Delta H°_{ads}$ (KJ.mol^{-1})	$\Delta S°_{ads}$ (J.mol^{-1}.K^{-1})
	Method 1		Method 2		Method 3	
303	-68.12	-90.4	-67.69	-89.04	-67.7	-89.93
313						-87.95
323						-88.51
333						-89.81

The negative value of $\Delta H°_{ads}$, reflects the adsorption of inhibitory molecules on the mild steel surface is an exothermic process and the calculation of the standard enthalpy of adsorption $\Delta H°_{ads}$ obtained by the Van't Hoff equation (Method2) [43]:

$$Ln\,K_{ads} = -\frac{\Delta H^{\circ}_{ads}}{RT} + constant \quad (15)$$

The Figure 11 shows a straight line from a plot of LnK_{ads} versus 1/T, the slope of the line is -Δ$H°_{ads}$/R, with (Δ$S°_{ads}$/R + ln1/C_{H2O}) is the interception. The values obtained of Δ$H°_{ads}$ and Δ$S°_{ads}$ are shown in Table 9.

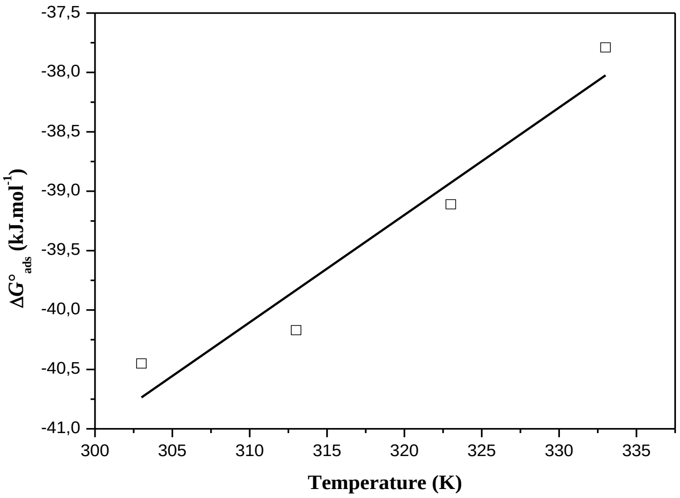

Figure 10: Variation of Δ$G°_{ads}$ to T on mild steel in 1M HCl solution containing the 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione

In order to evaluate the thermodynamic parameters (Δ$H°_{ads}$ and Δ$G°_{abs}$) by applying the Gibbs-Helmholtz equation (Method 3), which is the following [44]:

$$\left[\frac{\partial(\Delta G^{\circ}_{ads}/T)}{\partial T}\right]_p = -\frac{\Delta H^{\circ}_{ads}}{T^2} \qquad (16)$$

We can be arranged Equation (16) to obtain the following equation:

$$\frac{\Delta G^{\circ}_{ads}}{T} = -\frac{\Delta H^{\circ}_{ads}}{T} + constant \qquad (17)$$

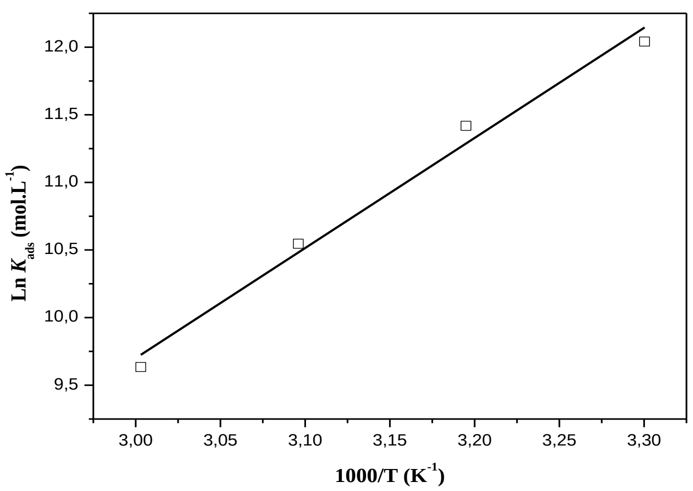

Figure 11: Van't Hoff plot of the mild steel of the 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione in a solution of 1 M HCl

We can deduce the values of Δ$H°_{ads}$ and Δ$S°_{ads}$ from the adsorption of the 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione on the surface of the steel. The figure 12 shows the plot of Δ$G°_{ads}$/T against 1000/T giving straight lines with slopes. In this case, the values of Δ$H°_{ads}$ and Δ$S°_{ads}$ obtained by the three methods are in good agreement (Table 9).

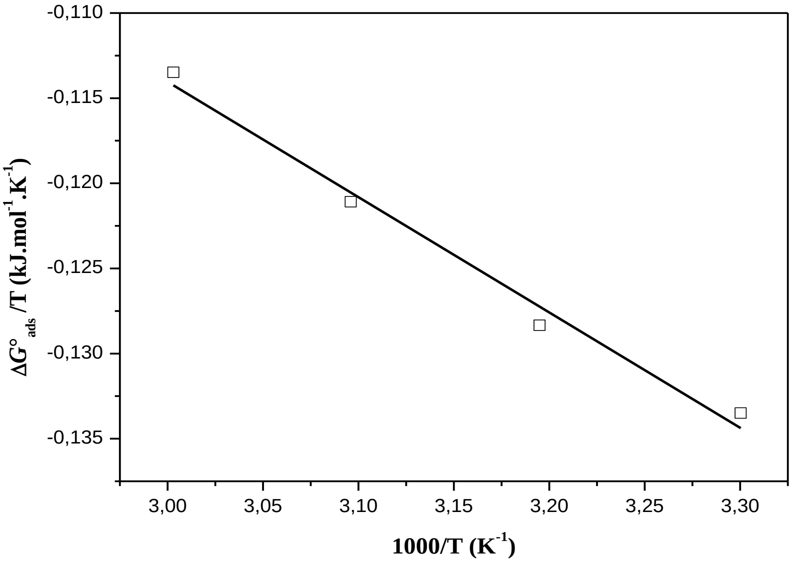

Figure 12: Relationship between $\Delta G°_{ads}$/T and the inverse of the absolute temperature

3.4. *Surface analysis by scanning electron microscopy (SEM)*

Mild steel surfaces morphologies exposed to1M HCl solution in the absence and presence of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione after 6 hours of immersion were examined by SEM Figure 13.

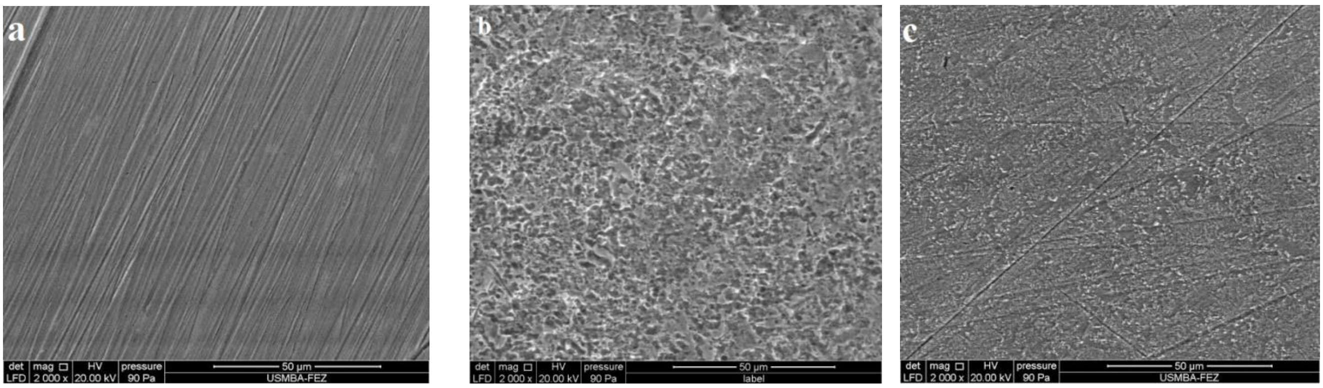

Figure 13: SEM micrographs of the carbon steel surface: (a) Metallic surface after being polished, (b) metallic surface after 6 h immersion in 1 M HCl and (c) metallic surface after 6 h immersion in 1 M HCl with 10^{-3} M of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione.

The parallel features on the surface of the mild steel prior to exposure to the etching solution of 1M HCl are clearly visible in Figure 13 (a), which are associated with the abrasive scratches. As regards the blank test, the mild steel sample shown in Figure 13(b) has been heavily damaged in the absence of 5-chloro-1- (2-(dimethylamino) ethyl)indoline2,3-dione indicated by the roughness of the surface as expected due to the corrosive attack of the acid solutions. However in the presence of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione Figure13(c) the rough surface is seen to decrease, the attack was uniform with no sign of corrosion selective, indicating an inhibitory effect of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione on the surface of the mild steel due to the formation of a protective film on the surface of the mild steel., with a slight evidence of the presence of adsorption on the metal surface.

Indeed, the product 5-chloro-1-(2-(dimethylamino)ethyl)indoline-2,3-dione has a strong tendency to adhere to the smooth surface of the steel and can be considered a good inhibitor corrosion of the steel in the normal hydrochloric medium.

Conclusion

All performed measurements showed that the 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dioneacts as a good inhibitor of the corrosion of mild steel in a hydrochloric acid solution, the inhibition efficiency increases with increasing concentration of the extract to the temperature 303K.
The 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione follows the Langmuir isotherm adsorption, it is due to the adsorption of organic molecules on the metal surface by charge transfer on the surface of the metal.
The inhibition efficiency of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione decreases proportionally with the increase in temperature from 303 to 343 K, and the addition of 1M HCl leads to an increase of the apparent activation energy E_a of the corrosion process, the calculated values of ΔG_{ads} indicate a strong and spontaneous adsorption on mild steel surface, the studies measured electrochemical analysis and weight loss and give similar results in good agreement.
Micrographs SEM show that the addition of 5-chloro-1- (2- (dimethylamino) ethyl)indoline-2,3-dione in 1M HCl in solution forms a film on the steel surface, which causes the decrease of the roughness of the metal surface and strongly protects the surface of the steel against corrosion.

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