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2-(2, 6-dichloranilino) phenyl acetic acid Drugs as Eco-Friendly Corrosion Inhibitors for Mild Steel in 1M HCl

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Expired declophen(2-(2, 6-dichloranilino) phenylacetic acid) ampoules were evaluated as non- toxic corrosion inhibitors for mild steel in 1 M HCl solutions, by chemical and electrochemical techniques, at different concentrations and temperature. The corrosion inhibition efficiency increased with increase in inhibitor concentration, but decreased with increase in temperature. Potentiodynamic polarization studies indicate that expired Declophen drugs acts as a mixed type inhibitor. The outcomes show that inhibition takes place by adsorption of the inhibitor on metal surface without altering the mechanism of corrosion process. The adsorption of Declophen takes place according to Langmuir`s adsorption isotherm. Thermodynamic parameters were calculated and discoursed. The data collected from the studied techniques are in good agreement to confirm the ability of using expired Declophen ampoules as corrosion inhibitors for steel in hydrochloric acid corrosive medium.

Keywords: Corrosion Inhibitors; Polarization; Steel; Expired Drugs; 2-(2, 6-dichloranilino) phenylacetic acid

1. INTRODUCTION

The major problem of mild steel is its dissolution in acidic medium, Corrosion of steel in acidic aqueous solutions is one of the major areas of concern in many industries where in acids are widely used for applications such as acid pickling, acid cleaning, acid descaling, and oil well acidizing. Because of general aggressiveness of acid solution the materials of construction are getting corroded easily. Steel corrosion is a thermodynamically feasible process as it is associated with decrease in Gibb’s free energy. Corrosion is an afflicting problem associated with every use of metals. The damage by corrosion results in high cost for maintenance and protection of materials used.

Development of methods to control corrosion is a challenge to scientists working in this area. Amongst various methods developed for corrosion protection, use of inhibitor is an attractive and most practical method for the protection of metals in contact with corrosion medium. Inhibitors reduce the corrosion of metallic materials by controlling the metal dissolution and consumption. Majority of the well-known inhibitors for the corrosion of steel in acidic medium are the organic compounds containing nitrogen, sulphur, oxygen atoms, or N-hetero cyclic compounds with polar groups. A large number of scientific studies have been devoted to the subject of corrosion inhibitors for mild steel in acidic media [1-12] Most of the commercial inhibitors are toxic in nature; therefore replacement by environmentally benign inhibitors is necessary Few non-toxic compounds have been investigated as corrosion inhibitors by some researchers [13-16].modified plastic waste was used as cheap and safe corrosion inhibitors for metals and alloys in different aqueous media [17-23] The use of pharmaceutical compounds offer interesting possibilities for corrosion inhibition due to the presence of hetero atoms like nitrogen, sulphur and oxygen in their structure and are of particular interest because of their safe use, high solubility in water and high molecular size. Some of the azosulpha and antimalarial drugs have been reported as good corrosion inhibitors [24-27], the use of piperazine derivative drug as a corrosion inhibitor has been reported [27].

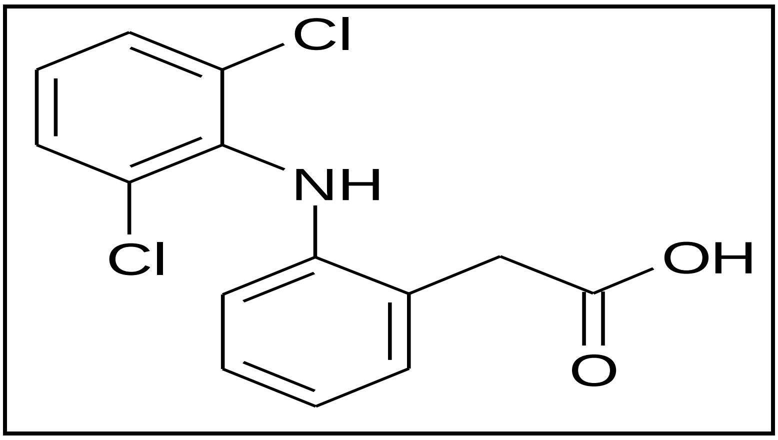
In the previous work expired drugs were investigated as corrosion inhibitor for Aluminum alloy and steel alloy in acidic medium [28-30].

In the present work expired Declophen has been investigated as corrosion inhibitor for mild steel in hydrochloric acid using weight loss, Open circuit potentiodynamic polarization techniques. The survey of literature reveals that, Declophen is a non-toxic pharmaceutical compound used as nonsteroidal anti-inflammatory agents and is used to treat Ankylosing Spondylitis, Aseptic Necrosis, Back Pain, Frozen Shoulder, Migraine, Muscle Pain, Osteoarthritis, Pain, Period Pain, Rheumatoid Arthritis, and Sciatica. Declophen is the commercial name of 2-(2, 6-dichloranilino) phenylacetic acid. Declophen containing N- atoms,O-atoms, and π- bond in aromatic system in its structure regarded as important factors for good inhibitor.

2. MATERIALS AND METHODS

2.1. Experimental procedure

The test material used was mild steel sample with the following composition (wt%): 0.18C, 0.6Mn, 0.05 S, 0.04 P, 0.1 Si and balance Fe. Test materials were abraded with different emery papers up to 1000 grade, cleaned with acetone, washed with double distilled water and properly dried prior to exposure. Analar grade HCl and double distilled water were used to prepare all solutions. Expired Declophen of (a molecular weight of 296) from (EIPICO) pharmaceutical company was used for the study. Figure (1. a) shows the molecular structure of ‘Declophen’.



2-(2, 6-dichloranilino) phenylacetic acid (DECLPHEN)

Figure 1.a. Molecular Structure of Declophen.

The chemical structure of the expired declophene was confirmed from their IR spectra. Figure (1.b) The presence of strong broad band at 3450cm^{-1}, indicates the termination of the compound with hydroxyl groups of the carboxylic end group and the band observed at 810cm^{-1} is assigned to –CH out-of-plane bending of substituted phenyl. This confirms the presence of phenyl rings in expired drugs.

The presence of strong bands at 1636 and 1155cm^{-1}, which were assigned for C O stretching and C–O stretching of carboxyl groups, the band observed at 2900 cm^{-1} for the aliphatic –CH2, appearance of a band at 3100cm−1, which represents NH stretching for secondary amine group in the structure of the expired dichlophen

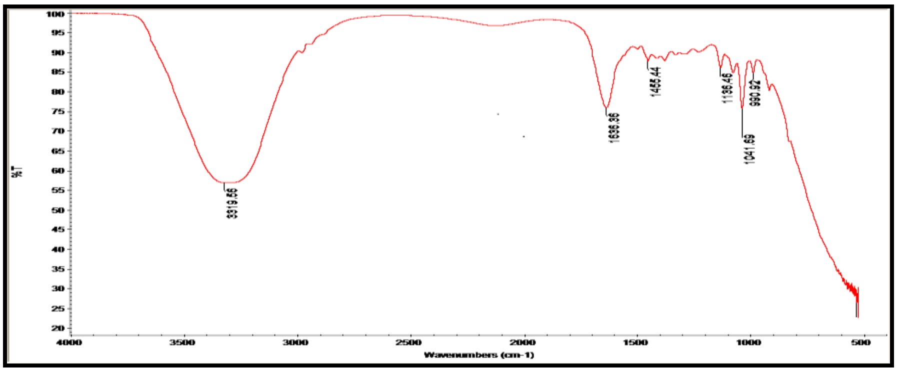


Figure 1.b. FT-IR Spectrum for expired Diclophen

2.2. Methods used to evaluate the corrosion and inhibition.

Weight loss measurements were performed on mild steel coupons having 2x2x0.2inch size, in 1M hydrochloric acid solution with different concentrations of the inhibitor. Weight loss of the metal coupons was noted after an immersing period of 7 days at the temperature range from 303 K to 333K.

the inhibition efficiency (I E%) and the degree of surface coverage (θ) were calculated from the equation (1) where W_0 and W_i are the values of weight loss without and with addition of inhibitor.

The potential of carbon steel electrodes was measured against the saturated calomel electrode (SCE) in 1M HCl solution in the absence and presence of various inhibitor concentrations until the open circuit potential is reached. Potentiodynamic polarization studies were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostat and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at a scan rate of 0.5 mVs^{-1} under static condition. A platinum electrode and saturated calomel electrodes (SCE) were used as auxiliary and reference electrodes, respectively. The working electrode was prepared from a cylindrical mild steel rod insulated with polytetrafluroethylene tape (PTFE). The area exposed to the aggressive solution was $1cm^2$. All the experiments were carried out at constant temperature of 30±1 ◦C.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

The weight loss results of mild steel in 1M HCl in the absence and presence of various concentrations of the inhibitor are summarized in Table (1). The I.E (%) and (θ) were calculated using the following equations:

$$\text{I.E }(\%) = \theta \times 100 \quad \text{where} \quad \theta = (W_0 - W_i / W_0) \qquad (1)$$

Where W_0 and W_i are weight loss of mild steel in the absence and presence of the inhibitor respectively. The inhibition efficiency increased with increase in the concentration of the inhibitor.

Table 1. Degree of surface coverage (θ) and percentage inhibition efficiency (%IE) of the used inhibitor in 1 M HCl at 303 K, obtained from weight loss measurements .

conc.(V %)	Wt. loss $mg.cm^{-2}$	Corrosion rate $mg.cm^2$ day-1	θ	%IE
BLANK	63.46	9	0	0
0.5 %	20.13	2.8	0.688	68.8
1.0 %	19.2	2.7	0.70	70
1.5 %	15.7	2.2	0.75	75
2.0 %	12.4	1.77	0.80	80
2.5 %	8.7	1.2	0.866	86.6

3.1.2. Effect of temperature

To elucidate the mechanism of inhibition and to determine the kinetic parameters of the corrosion process weight loss measurements were performed at 303, 313, 323, 333K. The effect of temperature on the corrosion inhibition efficiency of mild steel in the presence of the inhibitor is graphically represented in Figure (2).

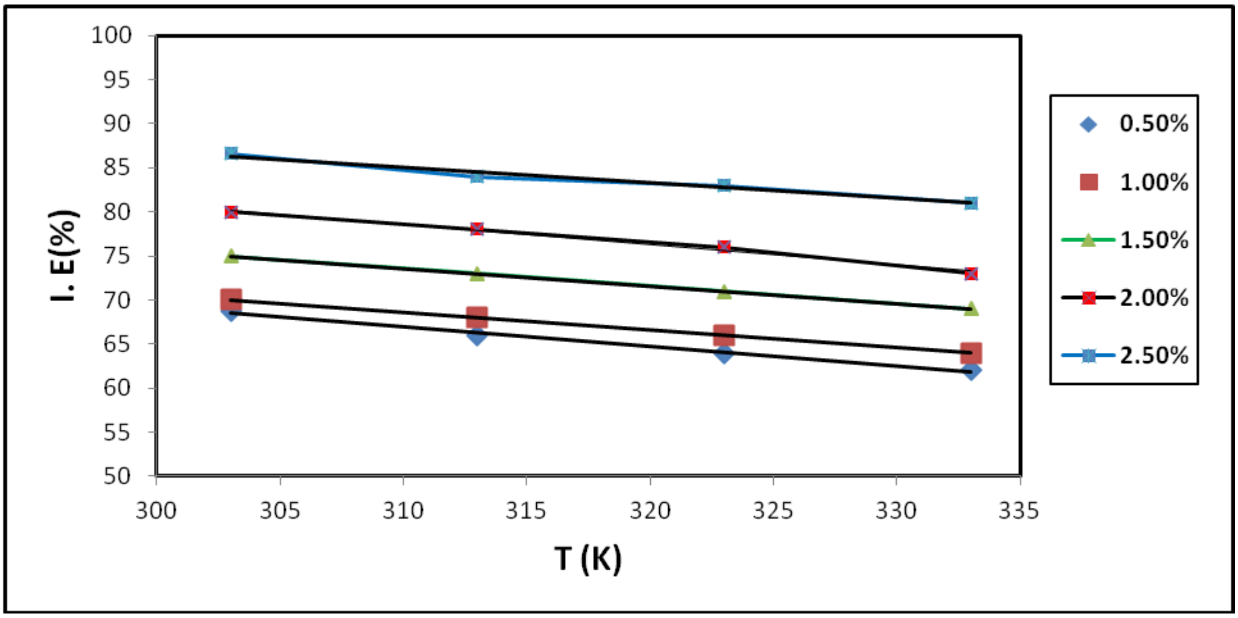


Figure 2. Effect of temperature on I.E for mild steel in 1M HCl in the presence of different concentrations of the used inhibitor.

The inhibition efficiency decreased with increase in temperature, leading to the conclusion that the protective film of these compounds formed on the mild steel surface is less stable at higher temperature; which may be due to the desorption of some adsorbed molecules from the surface of the mild steel at higher temperature due to which greater area of the metal is exposed to the acidic environment.

Table 2. Values of activation parameters for mild steel in 1M HCl in the absence and presence of different concentrations of the inhibitor

Inhibitor concentration (V %)	E_a (kJmol^{-1})	ΔH_a (kJmol^{-1})	$-\Delta S_a$ (J k^{-1} mol^{-1})
blank	41.4	41.1	154.3
0.5 %	53.8	50.5	159
1.0 %	57.4	54.12	156
1.5 %	58.6	58.7	150.8
2.0 %	61.5	62.7	147.8
2.5 %	65.5	65.7	143.7

The apparent activation energy (E_a) of metal corrosion in acid media can be calculated from the Arrhenius equation [31]:

$$\ln CR = (E_a/RT) + A \qquad (2)$$

where E_a is the apparent activation energy for the corrosion of mild steel , R is the universal gas constant, A is Arrhenius pre exponential factor and T is the absolute temperature. Figure(3) depicts the plot of log CR vs. 1/T and the values of E_a obtained from the slope of the plot are given in Table(2).

The higher value of activation energy (E_a) in the presence of inhibitor than in its absence is attributed to its chemisorption [30-32].

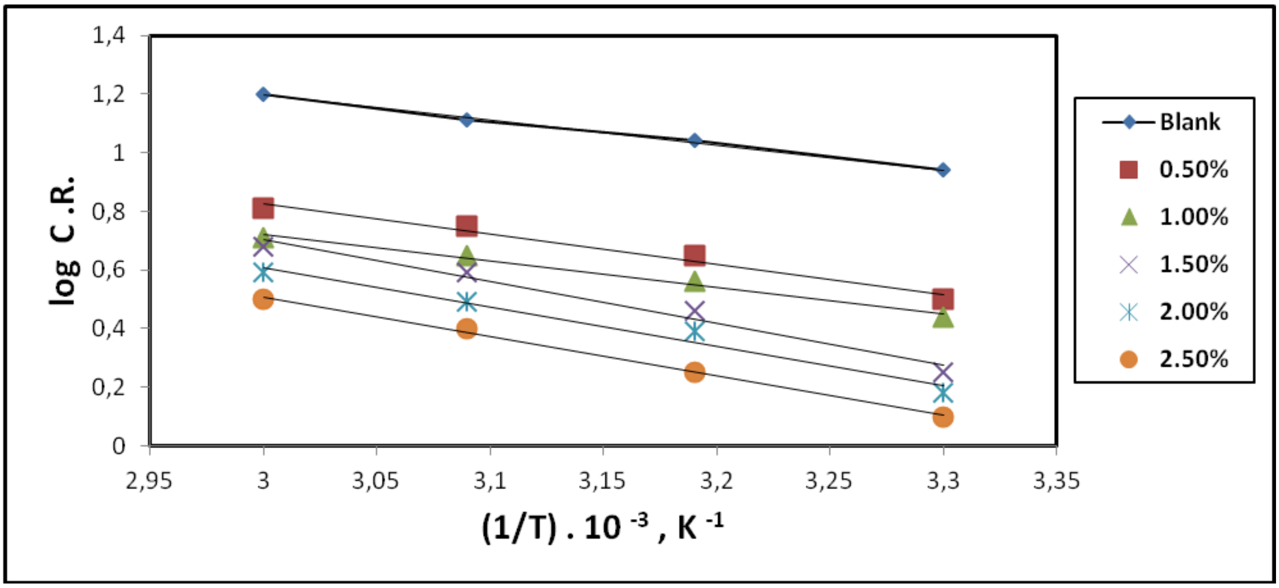


Figure 3. Arrhenius plot for mild steel in 1M HCl solution in the absence and presence of different concentrations of the inhibitor.

In the present study the higher value of E_a for mild steel in presence of expired Declophen compared to that in its absence is attributed to its chemical adsorption. Szauer and Brand [33] explained that the increase in E_a can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature and a corresponding increase in corrosion rates occurs due to the fact that greater area of metal is exposed to acid environment.

An alternative form of Arrhenius equation is the transition state equation [30, 31]:

$$CR = (RT/Nh) \exp(\Delta S_a/R) \exp(-\Delta H_a/RT) \qquad (3)$$

where, h is the Plank’s constant, N is the Avogadro’s number, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation. A plot of log (CR/T) vs. 1/T gave a straight line as shown in

Figure(4) with a slope of (-ΔH /2.303R) and an intercept of [log(R/Nh) + (ΔS /R)], from which the values of ΔH_a and ΔS_a were calculated and listed in Table 2.

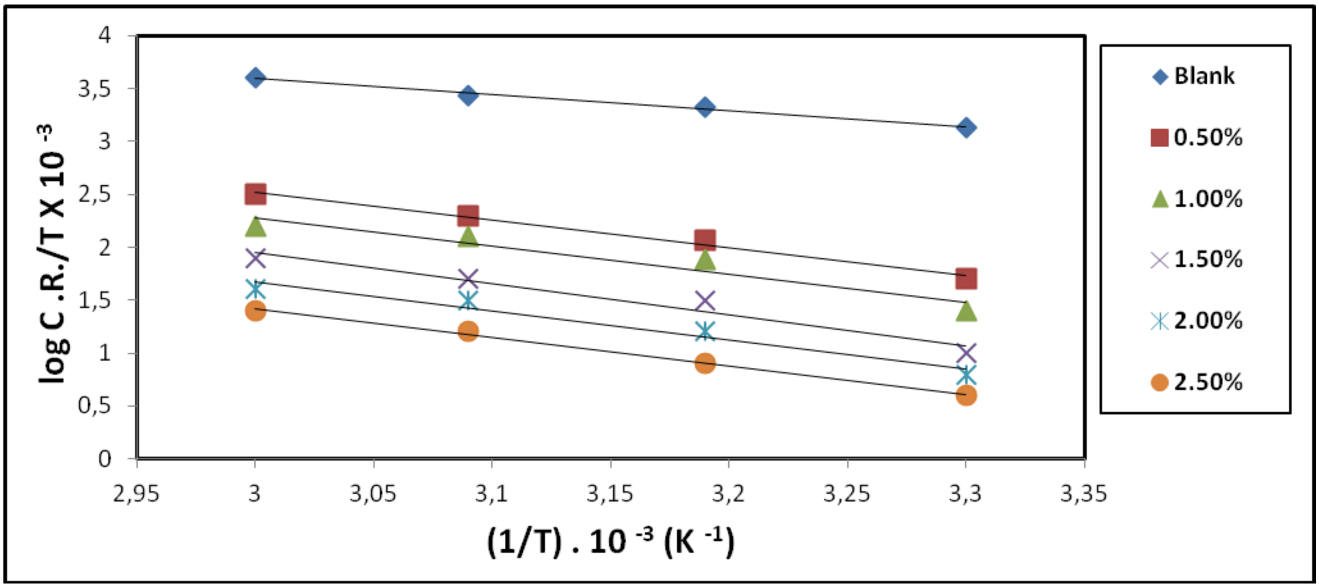


Figure 4. Transition state plot for mild steel in 1M HCl solution in the absence and presence of different concentrations of the inhibitor.

The positive values of ΔH_a for corrosion of mild steel in the presence and absence of the inhibitor reflect the endothermic nature of metal dissolution process. The increase in ΔH_a with increase in the concentration of the inhibitor for mild steel corrosion reveals that decrease in mild steel corrosion rate is mainly controlled by kinetic parameters of activation [32].

The entropy of activation values are less negative for inhibited solutions than that for the uninhibited solutions. This suggests that an increase in randomness occurred while moving from reactants to the activated complex [34].

3.1.3. Adsorption Isotherm and thermodynamic parameters

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the metal surface has to be known. The degree of surface coverage (ϴ) for different concentration of the inhibitor (C_i) has been evaluated. The data were tested graphically by fitting to various isotherms. A straight line with correlation coefficient nearly equal to 1.0 was obtained on plotting C_i/Θ against C_i as shown in Figure(5) suggesting, Adsorption of the compound on the mild steel surface followed Langmuir adsorption isotherm model. It is interpreted from the graph that, adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm at all studied temperatures.

According to this isotherm, the surface coverage (ϴ) is related [35] to inhibitor concentration C_{inhi} by equation (4)

$$C_{inhi} / \Theta = 1/ K_{ads} + C \qquad (4)$$

where, K_{ads} is equilibrium constant of the equilibrium adsorption process. This isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species.

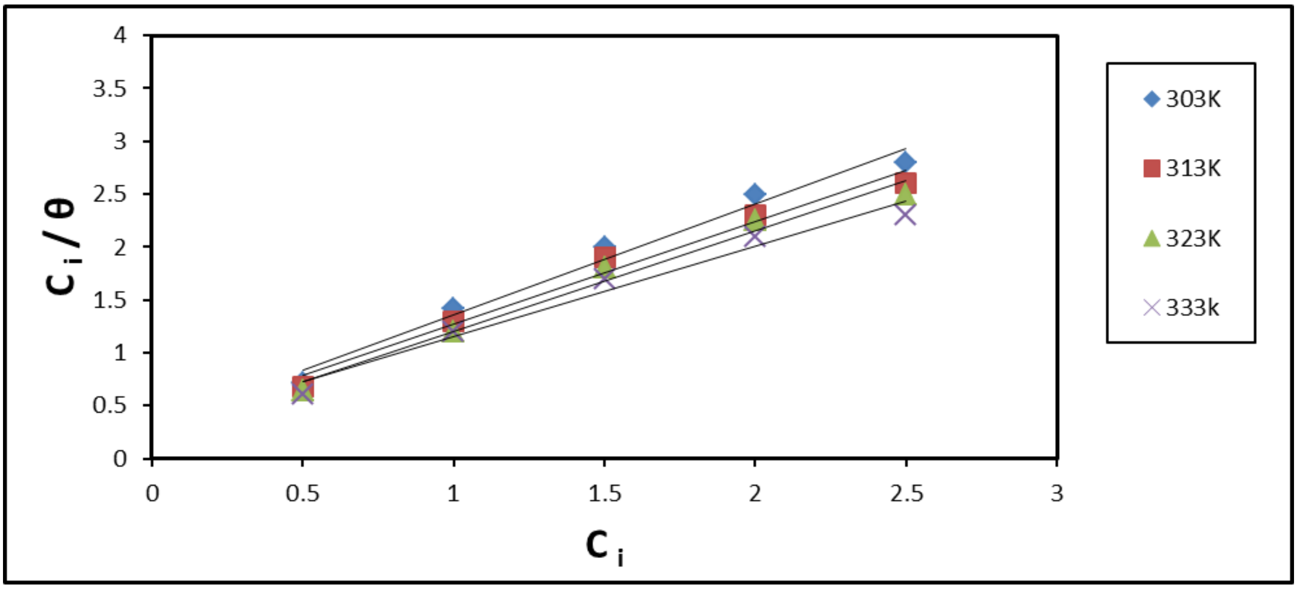


Figure 5. Langmuir adsorption isotherm for mild steel in 1M HCl solution at various temperatures.

The K_{ads} values can be calculated from the intercept lines on the C_{inhi}/Θ axis. This is related to the standard free energy of adsorption (ΔG_{ads}) by equation (5):

$$\Delta G_{ads} = -RT \ \mathrm{lin}(55.5 \ K_{ads}) \qquad (5)$$

where, R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/L. The values of ΔG_a for the inhibitor on the surface of mild steel are given in Table 3.

The negative value of ΔG_a indicated spontaneous adsorption of the inhibitor on the mild steel surface. Generally, the magnitude of ΔG_a around -20kJ/mol or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption). Those around -40kJ/mol or more negative are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions). In the present work, the calculated values ΔG° at 303K for mild steel is -41.5 kJ/mol, which indicate that adsorption of the inhibitor on the mild steel surface involves both physical and chemical process [36-39]. The enthalpy of adsorption (ΔH_{ads}) can be calculated from the rearranged Gibbs-Helmholtz equation:

$$\Delta G_{ads}/T = (\Delta H_{ads}/T) + K \qquad (6)$$

The variation of $\Delta G_{ads}/T$ with 1/T gave a straight line with a slope of ΔH_{ads} as shown in Figure(6). The entropy of adsorption ΔS_{ads} was calculated using the following thermodynamic equation:

$$\Delta S_{ads} = (\Delta H_{ads} - \Delta G_{ads})/T \qquad (7)$$

The calculated values of heat of adsorption and entropy of adsorption are listed in Table 3.

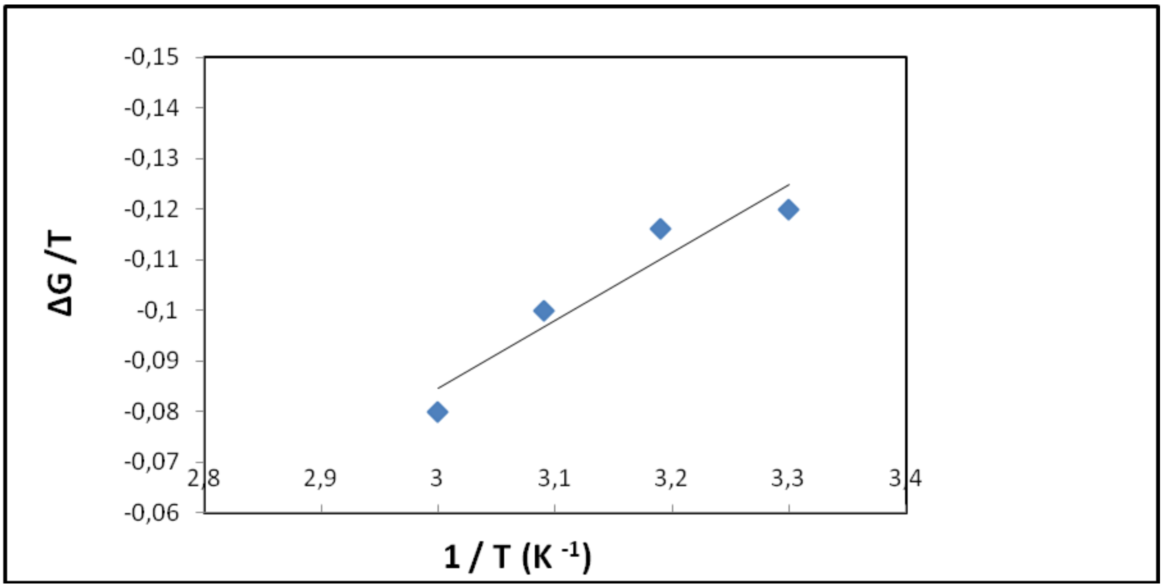


Figure 6. ΔG_{ads} /T versus 1/T plot for mild steel in 1M HCl solution.

Table 3. Values of thermodynamic parameters for the adsorption of the inhibitor in 1M HCl on the mild steel at different temperatures.

Temperature (K)	K (mol^{-1})	ΔG_{ads} ($kJmol^{-1}$)	ΔH_{ads} ($kJmol^{-1}$)	ΔS_{ads} ($J\ k^{-1}\ mol^{-1}$)
303	61009	-40.6	- 10.6	98.08
313	51801	-41.5	- 10.6	97.7
323	47290	-42.6	- 10.6	98.03
333	42123	-43.5	- 10.6	98.01

It is well known fact that adsorption is an exothermic phenomenon accompanied by a decrease in entropy [40]. In aqueous solutions the adsorption of the organic molecule is generally accompanied by desorption of water molecules [41].

$$\text{Inhibitor}_{(sol)} + x\,H_2O\,(ads) \rightleftarrows \text{Inhibitor}_{(ads)} + x\,H_2O_{(sol)}$$

The negative sign of ΔH_{ads} indicated the exothermic process of adsorption of the inhibitor on mild steel surface in HCl. The positive value of ΔS_{ads} in the presence of inhibitor can be attributed to the increase in the solvent entropy and more positive desorption entropy. It is also interpreted that the increase of disorderness is due to more water molecules which can be desorbed from the metal surface by one inhibitor molecule. Therefore it is revealed that decrease in the enthalpy is the driving force for the adsorption of the inhibitor on the surface of mild steel [42-45].

3.1.4. Corrosion Inhibition Mechanism

In hydrochloric acid medium, the metal surface is negatively charged due to the specifically adsorbed chloride ions on the metal surface.

$$Fe + Cl^{-} \longrightarrow (FeCl^{-})_{ads}$$

In acidic solution, the oxygen, and nitrogen atom of the Diclophen of the inhibitor can be protonated easily, due to high electron density on it, leading to positively charged inhibitor species. The adsorption can occur via electrostatic interaction between positively charged inhibitor molecule and negatively charged metal surface[28-31] leading to physisorpton of the inhibitor molecules. Further, co-ordinate bond may be formed between unshared e- pairs of unprotonated nitrogen atom of the inhibitor and vacant d-orbitals of metal surface atoms. Additionally inhibitor molecule may be chemically adsorbed due to interaction of π electrons of the benzene ring of the inhibitor with vacant d-orbitals of metal [37].

3.2. Open circuit potential measurements

The potential of mild steel electrodes immersed in 1 M HCl solution was measured as a function of immersion time in the absence and presence of expired Diclophen as shown in Figure(7) It is clear that the potential of mild steel electrode immersed in 1MHCl solution (blank curve) tends towards more negative potential firstly, giving rise to short step. This behavior was reported by another investigators [21, 23, 46],_which represents the breakdown of the pre-immersion air formed oxide film presents on the surface according to the following equation [30, 31]:

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$

This is followed by the growth of a new oxide film inside the solution, so that the potential was shifted again to more noble direction until steady state potential is established. Addition of inhibitor molecules to the aggressive medium produces a negative shift in the open circuit potential due to the retardation of the cathodic reaction.

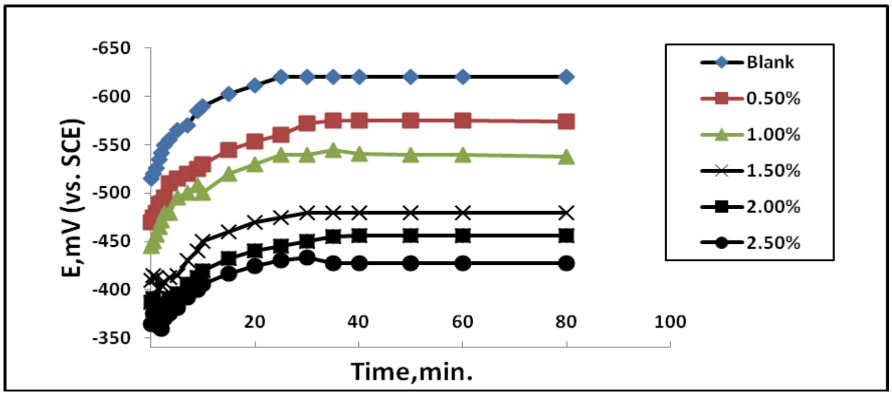


Figure 7. Potential–time curves for carbon steel immersed in 1M HCl solution in the absence and presence of expired Diclophen.

3.3. Potentiodynamic Polarization measurements

Polarization curves for mild steel in 1M hydrochloric acid without and with addition of different concentration of the inhibitor are shown in Figure(8). The values of electrochemical parameters associated with polarization measurements, such as corrosion potential (E_{corr}), corrosion current densities (i_{corr}), tafel slopes (βa,βc) and calculated inhibition efficiency (IE %) are listed in Table (4). The inhibition efficiency is given by the following equation [47-49]:

$$IE\ (\%) = 1 - (I_{inh} / I_{uninh}) \times 100 \qquad (8)$$

Where: I_{uninh} and I_{inh} are the corrosion current densities in the absence and presence of inhibitor respectively.

Table 4. Electrochemical parameters of mild steel in 1M hydrochloric acid solution at 303K.

inhibitor concentration (V %)	i_{corr} mA/cm^2	- E_{corr} mV	βa mV/decade	βc mV/decade	I.E(%)	Ө
blank	282	549	87	126	-	-
0.5 %	102	535	85	124	63.8	0.64
1.0 %	90	496	84	123	68	0.68
1.5 %	72	481	83	119	74	0.74
2.0 %	62	470	82	117	78	0.78
2.5 %	35	462	81	115	87.5	0.875

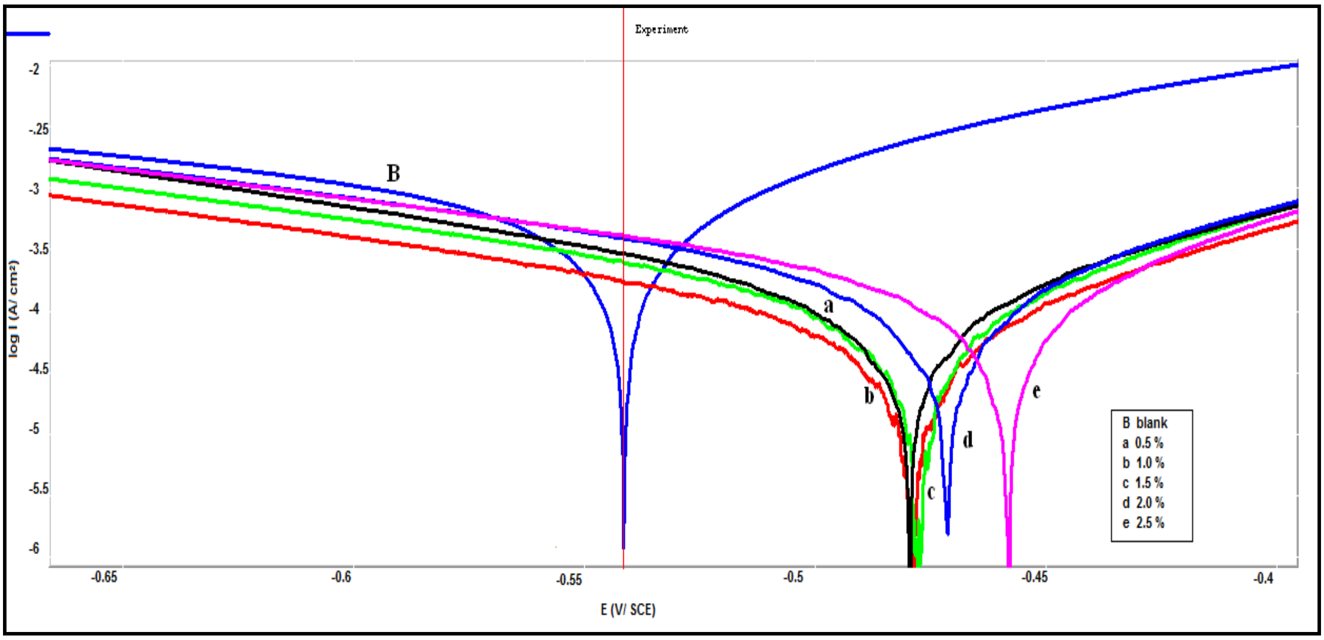


Figure 8. Potentiodynamic polarization curves of mild steel in 1M HCl solution at 30 ^{0}C containing various concentrations of Declophen inhibitor.

Corrosion current density decreased noticeably with increase in inhibitor concentration indicating, the increased inhibition efficiency with the increase in the concentration of the inhibitor. Generally, in acidic solution the anodic process of corrosion is the passage of metal ions from the solid metal to the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen molecules or reduction of oxygen. In the present study, the corrosion potential values slightly shifted to more positive value indicating addition of inhibitor molecule reduces both anodic dissolution and cathodic reduction; therefore, expired Diclophen could be classified as a mixed type inhibitor, but the anodic effect is more pronounced. The anodic and cathodic Tafel constants did not change significantly with increase in inhibitor concentration suggested that presence of inhibitor does not alter the reaction mechanism and inhibition effect has occurred due to simple blocking of the active sites [47-50], thereby reducing available surface area of the corroding metal.

4. CONCLUSION

1- Results obtained from the experimental data shows that expired Diclophen acts as a good inhibitor for the corrosion of mild steel in 1 M HCl.

2- The inhibition efficiency of Diclophen decreased with temperature, which leads to an increase in activation energy of corrosion process.

3- The adsorption of Diclophen follows Langmuir`s adsorption isotherm and The adsorption process is spontaneous and exothermic, accompanied by an increase of entropy.

4- Addition of inhibitor molecules to the aggressive medium produces a negative shift in the open circuit potential due to the retardation of the cathodic reaction.

5- Potentiodynamic polarization curves reveals that Diclophen is a mixed-type but predominantly anodic inhibitor.

6- The results obtained from different experimental studies are in good agreement.

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