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Electrochemical and Thermodynamic Investigation of Diclofenac Sodium Drug as a Potential Corrosion Inhibitor for Mild Steel in Hydrochloric Acid

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The performance of Diclofenac sodium (DS) drug as corrosion inhibitor for mild steel in 1 M HCl was investigated by weight loss and electrochemical methods. The inhibition efficiency of DS obtained by all methods was in good agreement with each other. Polarization studies revealed that the inhibiting action of the DS is mixed-type. The free energy of adsorption and the influence of temperature on the adsorption of inhibitor onto mild steel surface have been reported. The adsorption of the DS was found to obey the Langmuir adsorption isotherm.

Keywords: Mild steel; EIS; Corrosion; weight loss measurements

1. INTRODUCTION

It is commonly recognized that an organic inhibitor usually promotes formation of a chelate on a metal surface, by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption. In this way, the metal acts as an electrophile; and the nucleophile centers of inhibitor molecule are normally heteroatoms with free electron pairs that are readily available for sharing, to form a bond and thus decrease the corrosion rate. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. A number of compounds have been reported as corrosion inhibitors for mild steel in acidic environments. [1-8]

Despite the wide range of available organic compounds, the final choice of the inhibitor for a particular application is restricted by several factors, including increased environmental awareness and the need to promote environmentally friendly processes, coupled with the specificity of action of most acid inhibitors, which often necessitates the combined action of compounds to achieve effective corrosion inhibition. Consequently, there exists a need to develop inexpensive and environmentally friendly inhibitors. In recent years, researchers have paid attention to the development of drugs as inhibitors for the corrosion of metals in acid media. [9-13].

The aim of the present work is to study the Diclofenac sodium drug (DS) as corrosion inhibitor for mild steel in 1 M HCl solution using weight loss and electrochemical techniques. This drug is used as anti-inflammatory and analgesic. There is presently no report on use of Diclofenac sodium as a corrosion inhibitor in hydrochloric acid. The effect of temperature on different concentrations of inhibitor has been analyzed. Thermodynamic parameters obtained from the studies are also reported.

2. EXPERIMENTAL

2.1 Materials

The mild steel coupons of rectangular size (2.5 × 2.0 × 0.025) cm having the composition ; (wt %): C 0.17%; Mn 0.46%; Si 0.026%; Cr 0.050%; P 0.012%; Cu 0.135%; Al 0.023%; Ni 0.05%; and balance Fe were used for weight loss studies. Pretreatment of mild steel coupons included abrasion with emery paper as described previously [14]. Diclofenac sodium (DS) drug was procured from Cipla Pharmaceuticals Limited. The test solution 1 M HCl solution was prepared from analytical reagent.

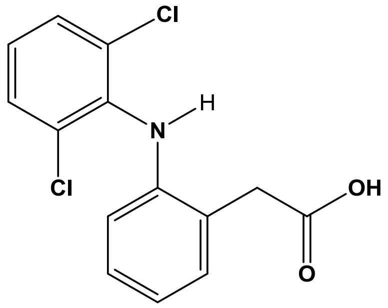

Figure 1. 2-(2-(2,6-dichlorophenylamino) phenyl)acetic acid (Diclofenac sodium)

2.2 Procedures

2.2.1 Weight loss measurements

For weight loss experiments, clean weighed metal rectangular coupons were immersed in 100 ml of 1 M HCl solution in conical flasks for 3 h at 308 K. These coupons were taken out, washed, dried, and weighed accurately with or without different concentration of DS. The inhibition efficiency and surface coverage (θ) was determined by using following equation:

$$\theta = \frac{w_0 - w_i}{w_0} \tag{1}$$

$$\eta_{\%} = \frac{w_0 - w_i}{w_0} \times 100 \tag{2}$$

where w_0 and w_i is the weight loss value in the absence and presence of inhibitor, respectively.

2.2.2 Electrochemical measurements

The electrochemical measurements were carried out using a Gamry Potentiostat/Galvanostat with a Gamry framework system based on ESA400. Gamry applications include software DC105 for corrosion, EIS300 for EIS measurements, and Echem Analyst version 5.50 software packages used for data fitting. These measurements were accomplished with a three electrodes cell assembly at constant temperature of 308 K. Mild steel coupons having exposed area 1.0 × 1.0 cm, was used as working platinum, and saturated calomel electrodes as used as counter electrode, and reference electrode respectively. All potentials were measured versus SCE. All the impedance measurements were performed under a potentiodynamic condition from 100,000 Hz to 0.01 Hz with amplitude of 10 mV peak-to-peak. The polarization measurements were performed by changing the electrode potential automatically from ¬250 to +250mV vs. OCP at a scan rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion current densities (I_{corr}). The linear polarization study was carried out from cathodic potential of −20mV vs. OCP to an anodic potential of +20mV vs. OCP at a scan rate 0.125mVs−1 to study the polarization resistance (Rp). The polarization resistance was calculated from the slope of curve in the vicinity of corrosion potential. Prior to the electrochemical measurements, the working electrode was immersed in 1.0 M HCl with and without addition of inhibitor for 30 minutes for stabilization of the OCP w.r.t. SCE.

3. RESULTS AND DISCUSSIONS

3.1 Weight loss studies

3.1.1 Effect of inhibitor concentration

The corrosion rate (C_r) in (mg cm^{-2} h^{-1}) was determined using the following equation:

$$C_r = \frac{w}{At} \tag{3}$$

where w is weight loss of coupons mild steel (mg), A the area of the coupon (cm^2), t is the exposure time (h). The value of inhibition efficiency and corrosion rate (C_r) obtained from weight loss method at different concentrations in 1 M HCl at 308 K temperature are presented in Tables 1.

Table 1. Parameters obtained from gravimetric measurements for mild steel in 1 M HCl containing different concentrations of DS at 308 K

Inhibitor	Concentration (mg/L)	Corrosion rate (mg cm^{-2} h^{-1})	Surface coverage (θ)	η (%)
Blank	0.0	7.00	--	--
DS	20	3.33	0.537	53.7
	60	1.30	0.819	81.9
	80	0.66	0.907	90.7
	100	0.33	0.953	95.3

From Table 1 it is clear that increase of inhibitor concentrations caused a decrease in the weight loss as well as corrosion rate of mild steel.

3.1.2. Effect of temperature

The effect of temperature on the inhibition efficiency of the DS for mild steel in 1 M HCl solution in the absence and presence of optimum concentration (100 mgL^{-1}) at temperature ranging from 308 to 338 K was investigated by weight loss measurements. The results obtained are given in Table 2 and plot between inhibition efficiency vs temperature is shown in Fig. 2.

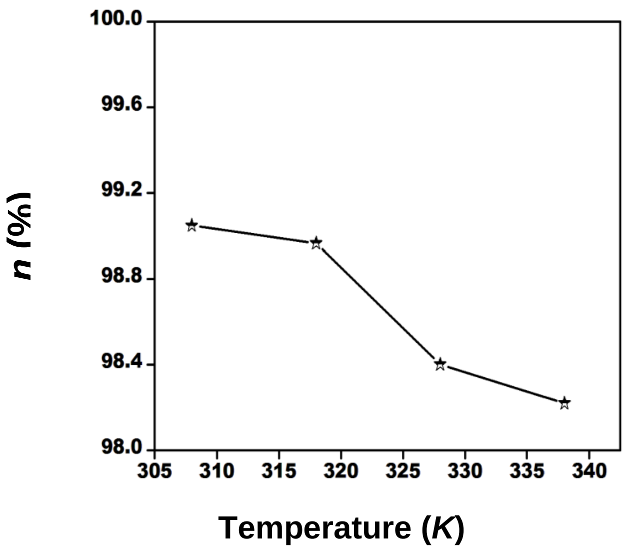

Figure 2. Variation of inhibition efficiency with Temperature

It is observed that as the temperature increases from 308 to 338 K inhibition efficiency decreases while corrosion rate increases. This behavior can be explained on the basis that the increase in temperature causes the desorption of the inhibitor molecules from the surface of mild steel.

3.1.3. Effect of time

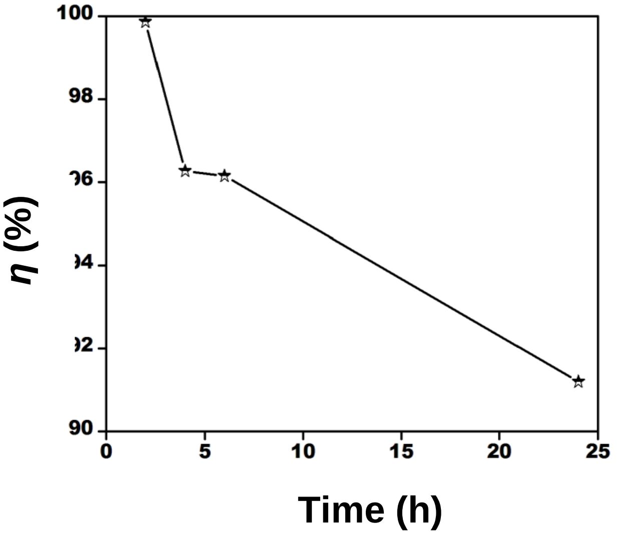

Figure 3. Variation of inhibition efficiency with Time

The effect of immersion time on the inhibition efficiency is shown in Figure 3.

From the figure it is observed that inhibition efficiency decreases from 99.86 to 91.20 with time.

3.1.4. Thermodynamic activation parameters

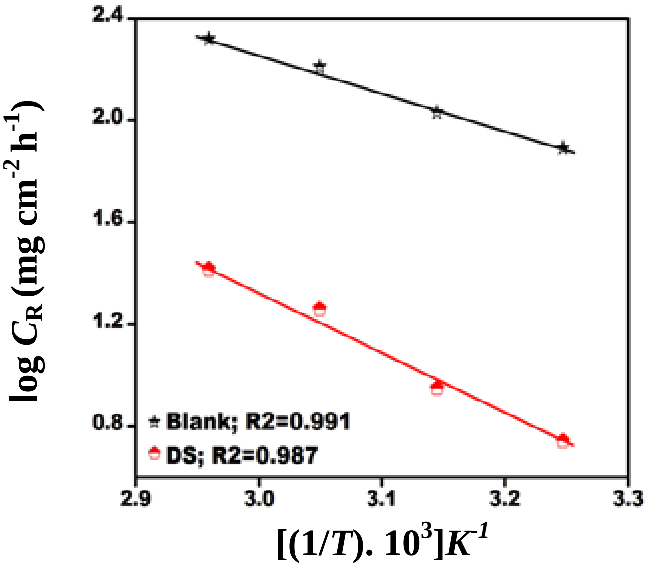

Figure 4. Arrhenius plot of mild steel in 1M HCl in absence and presence of different concentration of DS

In order to find the activation parameters of the corrosion inhibition process for mild steel in 1 M HCl solution, weight loss measurements were performed at a temperature range 308 K to 338 K in the absence and presence of 100 mgL^{-1} Diclofenac sodium. A plot of the logarithm of the corrosion rate (mg cm^{-2} h^{-1}) of mild steel vs. 1000/T gave a straight line as shown in Fig.4

According to the Arrhenius equation:

$$C_R = A\exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

where E_a is the apparent activation energy for the corrosion of mild steel in 1 M HCl solution, R molar gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The values of E_a obtained from the slope of the line (Fig. 4) are given in Table 2.

The straight lines were obtained according to the transition state equation:

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{H^*}{RT}\right) \tag{5}$$

where N is the Avogadro's number, h the Planck's constant, ΔH^* the enthalpy of activation and ΔS^* the entropy of activation.

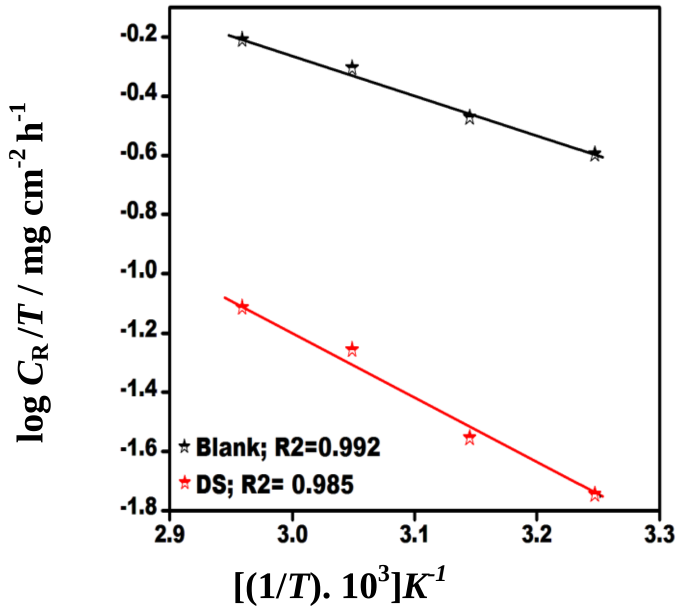

Figure 5. Transition-state plot of mild steel in 1 M HCl in absence and presence of optimum concentration of DS

Table 2. Thermodynamic parameters for mild steel in 1 M HCl in absence and presence of optimum concentration (100 mgL^{-1}) of DS (inhibitor)

Inhibitor	E_a ($kJmol^{-1}$)	$-\Delta G^o_{ads}$ ($kJ\ mol^{-1}$)				K_{ads} ($10^3\ M^{-1}$)				ΔH^* ($kJmol^{-1}$)	ΔS^* ($J\ K^{-1}mol^{-1}$)
		308	318	328	338	308	318	328	338		
Blank	27.9	--	--	--	--	--	--	--	--	25.4	-147.4
DS	46.4	41.53	41.46	41.27	40.22	118.84	107.93	73.82	2.54	85.5	65.49

Fig 5. shows that a plot of log (C_R/T) versus $1000/T$ gives a straight line with a slope of ($-\Delta H^*/2.303\ R$) and an intercept of log ($R/Nh + \Delta S^*/2.303\ R$) from which the values of $\Delta H^*$and $\Delta S^*$are calculated and are given in Table 2.

Table 2 shows that value of enthalpy of activation is positive and higher in presence of inhibitor. The positive sign of ΔH^*reflects the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow. The entropy of activation $\Delta S^*$is higher (65.49K^{-1} mol^{-1}) in the presence of inhibitor than that (-147.4J K^{-1} mol^{-1}) in the absence of the inhibitor. This is opposite to what would be expected, since adsorption of inhibitor is an exothermic process and is always accompanied by a decrease of entropy. The reason could be explained as follows: the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compound in the aqueous phase [$Org_{(sol)}$] and water molecules at the electrode surface [$H_2O_{(ads)}$]. In this situation, the adsorption of organic inhibitor is accompanied by desorption of water molecules from the surface. Thus, while the adsorption process for the inhibitor is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent. The thermodynamic values obtained are the algebraic sum of the adsorption of organic molecules and desorption of water molecules. Therefore, the gain in entropy is attributed to the increase in solvent entropy [15]. The positive values of ΔS^*means that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of inhibitor onto the mild steel surface [16].

3.1.5. Adsorption considerations

The standard free energy of adsorption (ΔG°_{ads}) at different temperatures is calculated from the equation:

$$\Delta G^{o}_{ads} = -RT \ln(55.5 K_{ads}) \tag{6}$$

where the value 55.55 is the concentration of water in solution expressed in M [17-18] and K_{ads} is equilibrium adsorption constant and is given by:

$$K_{ads} C = \frac{\theta}{1-\theta} \tag{7}$$

where θ is degree of surface coverage of the mild steel surface and C the molar concentration of inhibitor.

The values of K_{ads} and ΔG°_{ads} for mild steel in 1 M HCl solution in the presence of 100 mgL^{-1}DS is given in Table 2.

The negative values of ΔG^{o}_{ads} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. Generally, values of ΔG^{o}_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and charge metal, such as physisorption. When it is around -40 kJ mol^{-1}or higher values it involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond that is chemisorption [19-20]. The calculated values range from -40.22 to-41.53 kJmol^{-1} (Table 2). This indicates that DS are adsorbed chemically on mild steel surface in 1 M HCl solution. The unshared electron pairs of heteroatom interact with d-orbital of iron atom of steel to provide a protective chemisorbed film [21].

Attempts were made to fit θ values to the Freundlich, Temkin, Langmuir, and Flory- Huggins isotherms, and the correlation coefficient (R^2) values were used to determine the best fit isotherm. The best results were obtained for the Langmuir adsorption isotherm. A straight line was obtained on plotting C/θ vs. C (mol L^{-1}) as shown in Fig 6.

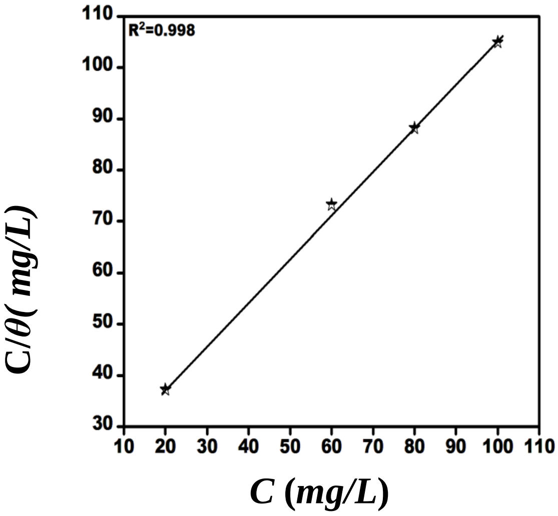

Figure 6. Langmuir's isotherm for adsorption of DS on mild steel surface in 1 M HCl

It suggested that the adsorption of the inhibitor at the metal/ solution interface follows Langmuir's adsorption isotherm.

3.2. Electrochemical measurements

3.2.1. AC technique: Electrochemical impedance spectroscopy

AC impedance results of mild steel/hydrochloric acid interface obtained in the absence and presence of various concentrations of DS in the form of Nyquist plots are shown in Fig 7.

The Nyquist plots for DS are characterized by one semicircular capacitive loops. The corrosion process is two steps as in any electrochemical process. First, the oxidation of the metal (charge transfer process) and second, the diffusion of the metallic ions from the metal surface to the solution (mass transport process). Inhibitors get adsorbed on the electrode surface and thereby produce a barrier which inhibits corrosion [22].

It must be noted that the capacitive loops are depressed ones with centers under the real axis even though they have a semicircle appearance. This kind of deviations is mostly referred to as frequency dispersion which is attributed to irregularities and heterogeneities of the solid surfaces [23].

In the real corrosion systems, the metal/solution interface double layer does not behave as a real capacitor.

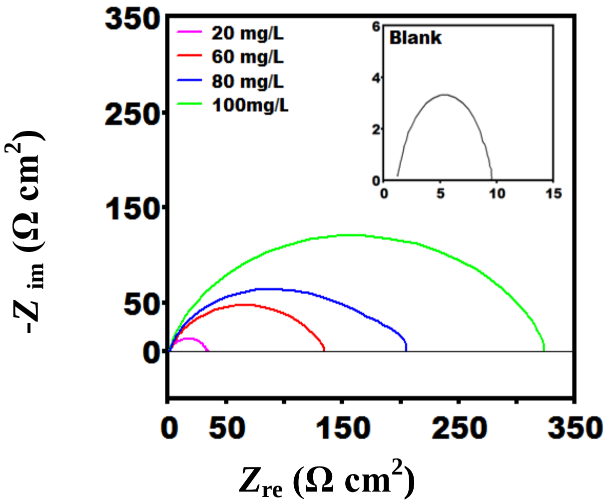

Figure 7. Nyquist plots for mild steel in 1 M HCl in absence and presence of various concentrations of DS at 308 K

The charge distribution is controlled by electron on the metal side of the double layer, whereas it is controlled by ions on the solution side [24] The high frequency (HF) part of the impedance and phase angle reflects the behavior of heterogeneous surface layer, whereas the low frequency (LF) part shows the kinetic response for the charge transfer reaction [25]. A small inductive loop can be seen for both uninhibited and inhibited solutions (Fig.7). The presence of this low frequency inductive loop may be attributed to the relaxation process obtained by adsorption of species like $(Cl^-)_{ads}$ and $(H^+)_{ads}$ on the electrode surface [26]. The simplest model as shown in Fig 8.

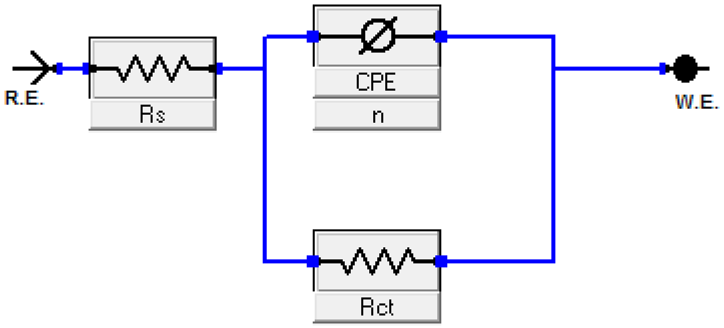

Figure 8. Equivalent circuit used to fit the EIS data

This consist of the solution resistance, R_s, in series with the parallel combination of constant phase element (CPE) in place of double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}).

Mathematically, a CPE's impedance is given by

$$Y_{\mathrm{CPE}} = Y_0 (j\omega)^n \tag{8}$$

where Y_0 is the amplitude comparable to a capacitance, j is the imaginary unit, ω is the angular frequency ($\omega = 2\pi f$, the frequency in Hz), and n is the phase shift which gives details about the degree of surface in homogeneity. The CPE can be expressed by the values of n if resistance (n=0, $Y_0 = R$), capacitance (n=1, $Y_0 = C$), inductance (n= -1, $Y_0 = L$) and Warburg impedance (n=0.5, $Y_0 = W$) [27]. The impedance data are given in Table 3.

Table 3. Electrochemical Impedance Spectroscopy measurements on mild steel electrode in 1 M HCl in absence and presence of different concentration of DS at 308 K

Inhibitor	R_s (Ω)	R_{ct} (Ω cm^2)	n	Y_0 (μFcm^{-2})	C_{dl} (μFcm^{-2})	θ	η (%)
Blank	0.58	13.56	0.798	481.2	137.95	--	--
20	1.07	31.41	0.858	56.1	29.4	0.795	79.5
60	1.30	129.8	0.816	72.5	25.8	0.912	91.2
80	0.969	180.1	0.831	66.8	24.5	0.961	96.1
100	0.832	321.6	0.856	35.4	15.3	0.980	98.0

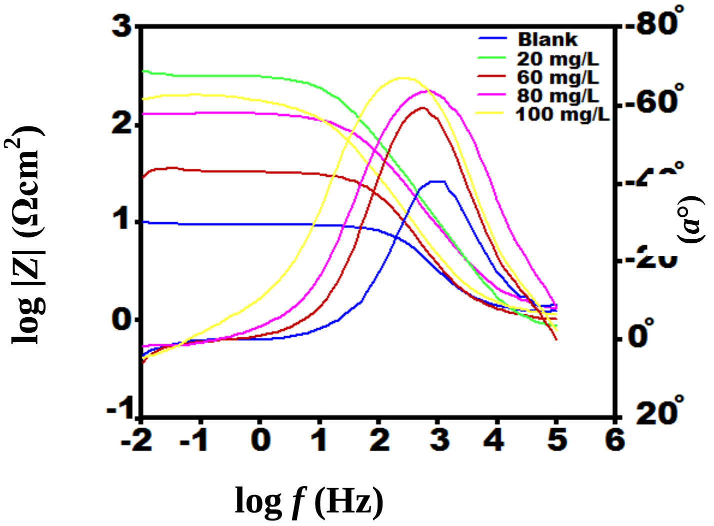

Figure 9. Bode impendence plots for mild steel in 1 M HCl in absence and presence of various concentrations of DS at 308K

Table 3 shows that the addition of the DS in 1 M HCl increases the inhibition efficiency, charge transfer resistance and decreases the double layer capacitance (C_{dl}) given as [28];

$$C_{\mathrm{dl}} = \frac{\varepsilon\varepsilon_0}{d} A \tag{9}$$

where ε_0 is the vacuum dielectric constant, ε is the local dielectric constant, d is the thickness of the double layer, and A is the surface area of the electrode. It is obvious that the decrease in the C_{dl}

values occurs due to the adsorption of DS molecule on the metal surface. Decrease in the capacitance, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, strongly suggests that the inhibitor molecules are adsorb at the metal/solution interface.

Fig. 9 shows the Bode phase angle plots recorded for mild steel electrode immersed in 1 M HCl in the absence and presence of various concentrations of DS at its open circuit potential.

The values of Bode impedance magnitude (S) and maximum phase angles (a°) are listed in Table 4.

Table 4. The slopes of the Bode impedance magnitude plots at intermediate frequencies (S) and the maximum phase angles (α) for mild steel in 1 M HCl solution at different concentrations of DS at 308 K

Inhibitors	$-S$	$-\alpha^{\circ}$
Blank	0.502	40.90
25	0.788	63.02
50	0.750	66.78
75	0.707	65.66
100	0.790	70.67

In the intermediate frequency region, a linear relationship between log $|Z|$ against log f, with slope near -1 and the phase angle tends to become -90°, can be observed. This response is a characteristic of capacitive behavior. An ideal capacitive response would result in a slope of -1 and a phase angle of -90°; however, it is well known that an electrochemical system generally does not behave in an ideal manner [29]. In our case, in intermediate frequencies region, a linear relationship between log $|Z|$ vs. log f with a slope near -0.80 and the phase angle approaching -80° has been observed. These deviations considered to be the deviation from the ideal capacitive behavior at intermediate frequencies. The Bode phase angle plots show single maximum (one time constant) at intermediate frequencies, broadening of this maximum in presence of DS account for the formation of a protective layer on electrode surface [30].

3.2.2. Potentiodynamic polarization

Polarization curves for mild steel at various concentrations of DS in are shown in Fig. 10.

It is clear from the potentiodynamic curves that the presence of DS, in acid solution, decreases the corrosion rate. The decrease in I_{corr} value is due to the adsorption of the inhibitor molecules. It is observed that both the cathodic and anodic reactions are suppressed with the addition of DS which suggest it inhibit both anodic dissolution and cathodic hydrogen evolution reaction. Electrochemical corrosion parameters i.e. corrosion potential (E_{corr}), cathodic and corrosion current density (I_{corr}) obtained from the Tafel extrapolation of the polarization curves along with inhibition efficiency are given in Table 5.

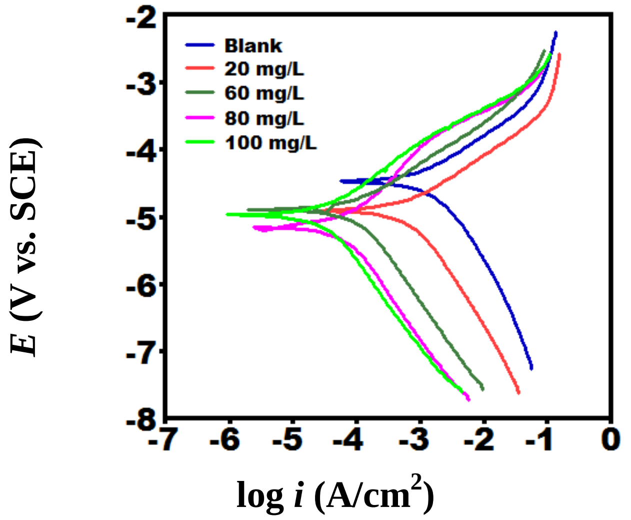

Figure 10. Potentiodynamic polarization curves for mild steel in 1 M HCl in absence and presence of various concentrations of DS at 308 K

Table 5. Electrochemical impedance Spectroscopy measurements on mild steel electrode in 1 M HCl in absence and presence of different concentration of DS at 308 K

Inhibitor mgL^{-1}	I_{corr} (µA/cm)	E_{corr} (mV/ SCE)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	θ	η (%)
Blank	892	-444	61.0	81.0	--	--
25	301	-490	54.6	185.0	0.662	66.2
50	117	-498	57.8	151.0	0.868	86.8
75	92.3	-506	60.5	147.0	0.896	89.6
100	25.5	-505	69.1	138.2	0.971	97.1

The inhibition efficiency η % was calculated using the following equation:

$$\eta_{\%} = \frac{I^{0}_{\text{corr}} - I^{\text{i}}_{\text{corr}}}{I^{0}_{\text{corr}}} \times 100 \qquad (10)$$

where, $I°_{\text{corr}}$ and $I^{\text{i}}_{\text{corr}}$ are the corrosion current density in absence and in the presence of DS, respectively. There was no significant change in the E_{corr} values in the presence of DS which suggest that it is mixed type inhibitor [31-32].

The values of β_c changed significantly with increasing DS concentrations, which indicated the effect of the compound on the kinetics of hydrogen evolution [33]. Compared with the blank, the anodic curves of the working electrode in the acid solution containing DS shifted obviously to the direction of the current reduction, which implied that the DS could also suppress the anodic reaction. Only as the change in E_{corr} value was more than 85 mV, a compound could be recognized as an anodic or a cathodic type inhibitor [34]. The largest displacement of E_{corr} was about 61mV (Table 5). Therefore, DS might act as a mixed-type inhibitor. Corrosion is an electrochemical phenomenon and inhibitors decrease the velocity of electrochemical electrode reactions. A lower I_{corr} value for DS solutions implies that the rate of electrochemical reactions was reduced due to the formation of a barrier layer over the mild steel surface by the DS molecules [35].

3.3. Mechanism of inhibition

The corrosion inhibition of mild steel in hydrochloric acid solution by Diclofenac sodium can be explained on the basis of adsorption as depicted in Figure 11.

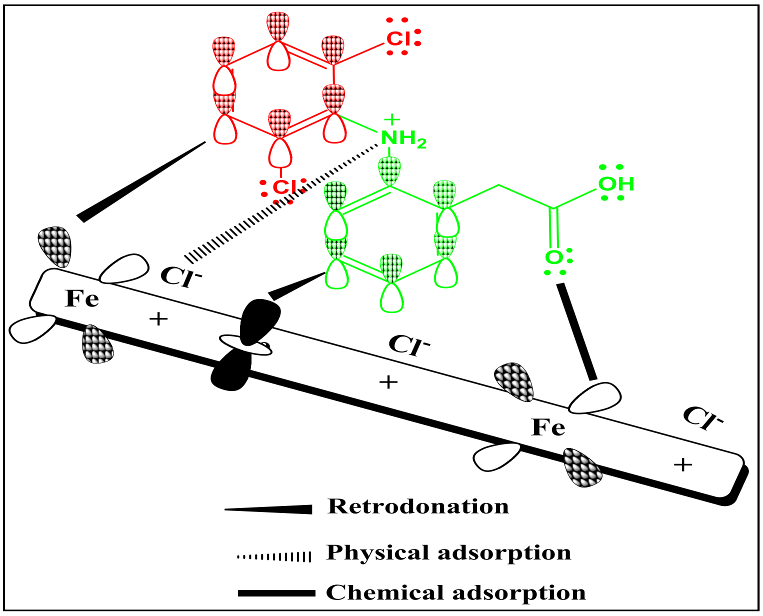

Figure 11. Mechanism of inhibition

There is interaction occours between inhibitor molecules and mild steel surface:

(a) Protonated inhibitor molecules with already adsorbed chloride ions (Physical adsorption)

(b) Interaction of lone pair of electron of N atoms or π electrons of aromatic ring with vacant d-orbitals of the surface Fe atoms (Chemical adsorption).

(c) Interaction of d-electrons of Fe with the high energy orbitals of inhibitor molecules (Reterodonation)

4. CONCLUSIONS

1. The results obtained from different measurements such as weight loss, EIS and polarization measurements showed that Diclofenac sodium inhibits corrosion of mild steel in 1 M HCl and these studies gave consistent results.
2. The adsorption of Diclofenac sodium on mild steel surface is found to obey the Langmuir adsorption isotherm and they are mixed-type inhibitors.
3. Adsorption of Diclofenac sodium on the mild steel surface was a typical chemisorption.

4. Tafel curves showed that Diclofenac sodium is a mixed type inhibitor.

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References

1. M.A. Quraishi, R. Sardar, *Corrosion* 58 (2002) 103
2. F. Bentiss, M. Lebrini, M. Lagrenée, *Corros. Sci.* 47 (2005) 2915
3. E. Norr, *Corros. Sci.* 47 (2005) 33
4. M. Lebrini, M. Lagrenee, H. Vezin, L. Gengembre, F. Bentiss, *Corros. Sci.* 47 (2005) 485
5. A.S. Fouda, A.S. Ellithy, *Corros. Sci.* 51 (2009) 868
6. Z. Ait Chikh, D. Chebabe, A. Dermaj, N. Hajjaji, A. Srhiri, M.F. Montemor, M.G.S. Ferreira, A.C. Bastos, *Corros. Sci.* 47 (2005) 447
7. X.L. Cheng, H.Y. Ma, S. Chen, R. Yu, X. Chen, Z.M. Yao, *Corros. Sci.* 41 (1999)
8. C. Kustu, K.C. Emregul, O. Atakol, *Corros. Sci.* 49 (2007) 2800
9. M Abdalla, *Corros. Sci.* 46 (2004) 1981
10. I Ahamad; MA Quraishi, *Corros. Sci.* 52 (2010) 651
11. SK Shukla; AK Singh; I Ahamad; MA Quraishi, *Mater. Lett.* 63 (2009) 819
12. I Ahamad; R Prasad; MA Quraishi. *J.Solid State Electrochem.*14 (2010) 2095
13. I. Ahamad, S. Khan, K. R. Ansari and M. A. Quraishi, *J. Chem. Pharm. Res.* 3 (2011) 703
14. S. K. Shukla and M. A. Quraishi, *Mater. Chem. Phys.* 120 (2010) 142.
15. B. Ateya, B. El-Anadauli, F. El Nizamy, *Corros. Sci.* 24 (1984) 509
16. XH .Li, SD. Deng, GN. Mu, H. Fu, FZ .Yang, *Corros. Sci.* 50 (2008) 420
17. X. Li, S. Deng, H. Fu, T. Li, *Electrochim. Acta.* 54 (2009) 4089
18. E. Cano, JL. Polo, A. La Iglesia, JM. Bastidas, *Adsorption.* 10 (2004) 219
19. A. Yurt, A. Balaban, S. Ustün Kandemir, G. Bereket and B. Erk, *Mater. Chem. Phys.* 85 (2004) 420
20. A. K. Singh and M. A. Quraishi, *Corros. Sci.* 52 (2010) 1373
21. A. K. Singh and M. A. Quraishi, *Corros. Sci.* 52 (2010) 1529
22. A.K. Satpati, P.V. Ravindran, *Mater. Chem. Phys.* 109 (2008) 352
23. K. Juttner, *Electrochim. Acta*. 35 (1990) 1501
24. M. Ozcan, I. Dehri, M .Erbil, *Appl. Surf. Sci.* 236 (2004) 155
25. MS. Morad, *Corros. Sci.* 42 (2000) 1307
26. HH. Hassan, E. Abdelghani, MA. Amin, *Electrochim. Acta* .52 (2007) 6359
27. M.A. Quraishi, K.R Ansari, D. K. Yadav, Eno E. Ebenso, *Int. J. Electrochem. Sci.* 7 (2012) 12301
28. EE. Oguzie, Y. Li, FH. Wang , *Electrochim. Acta.* 53 (2007) 909
29. H. H. Hassan, *Electrochim. Acta*. 53 (2007) 1722
30. D. K. Yadav, M. A. Quraishi and B. Maiti, *Corros. Sci.* 55 (2012) 254
31. M.A. Quraishi, M.Z.A. Rafiquee, S. Khan and N. Saxena, *J. Appl. Electrochem.* 37 (2007) 1153
32. I. Ahamad, R. Prasad and M.A. Quraishi, *J. Solid State Electrochem.* 14 (2010) 2095
33. W. Li, Q. He, C. Pei, B. Hou, *Electrochim. Acta.* 52 (2007) 639
34. H. Ashassi-Sorkhabi, M.R. Majidi and K. Seyyedi, *Appl. Surf. Sci.* 225 (2004) 176
35. K. S. Jacob and G. Parameswaran, *Corros. Sci.* 52 (2010) 224