

# Corrosion Inhibition of Mild Steel in 0.5 M HCl Using a Hydrazide Derivative as Inhibitor

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**Abstract** -The inhibition behaviour of N'-[4-(dimethylamino) benzylidene]-4-hydroxybenzo hydrazide (DABBH) on the corrosion of mild steel in 0.5 M hydrochloric acid was studied by Tafel polarization technique and electrochemical impedance spectroscopy technique. The inhibition efficiency of DABBH increased with the increase in its concentration and increase in temperature. Polarization study showed that DABBH acts as a mixed type inhibitor and its adsorption on mild steel surface was found to follow Langmuir's adsorption isotherm. The formation of protective film was confirmed by scanning electron microscopy study.

**Keywords-** corrosion inhibition, mild steel, Tafel polarization, EIS, acid medium

## I. Introduction

Mild steel in acid solution is widely used in various industrial processes and corrosion of mild steel known to occur in this environment. Acidic solutions are extensively used in acid cleaning, pickling, and descaling processes, as well as for drilling operations in oil and gas exploration [1]. The use of inhibitors is the most practical and economical methods for the corrosion protection and prevention of unexpected metal dissolution in aqueous aggressive media [2]. The aim of the present work is to introduce a new hydrazide derivative, N'-[4-(dimethylamino) benzylidene]-4-hydroxybenzo hydrazide (DABBH) as corrosion inhibitor for mild steel in 0.5 M hydrochloric acid medium.

## II. Experimental

**Materials:** The mild steel specimen used has the chemical composition (wt. %): C: 0.159; Si: 0.157; Mn: 0.496; P: 0.060; Cr: 0.047; Ni: 0.06; Mo: 0.029; Al: 0.0043; Cu: 0.116; the rest Fe. The working specimens were prepared in the form of a cylindrical rod embedded in epoxy resin, having one end of the rod with an open surface area of 0.95 cm<sup>2</sup>. Polishing of the exposed surface was done using emery papers of different grades (400-1000). Further the polishing was done with disk polisher using levigated alumina to obtained mirror finish and finally washed with double distilled water, rinsed with acetone, and dried.

The standard solution of 0.5 M hydrochloric acid was prepared using AR grade hydrochloric acid and double distilled water.

N'- [4-(dimethylamino) benzylidene]-4-hydroxy benzohydrazide (DABBH) was synthesized as per the

reported literature [3]. Figure 1. represents the chemical structure of the inhibitor molecule. The product obtained was purified by recrystallization and characterized by IR spectroscopy (Schinadzu FTIR 8400S Spectrophotometer).

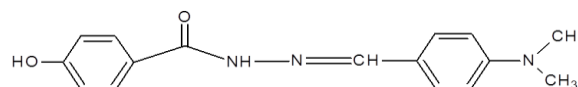


Figure 1. Chemical structure of DABBH

**Electrochemical measurements:** Electrochemical measurements were carried out using an electrochemical work station (CH Instrument USA model 604D series with beta software). The electrochemical cell consisted of a conventional three-electrode Pyrex glass cell with platinum electrode as counter electrode, saturated calomel electrode (SCE) as reference electrode, and mild steel as working electrode. Freshly polished mild steel specimen with surface area of 0.95 cm<sup>2</sup> was exposed to 0.5 M HCl medium in the absence and presence of inhibitor at temperatures of 30 to 60 °C. The steady state open circuit potential (OCP) with respect to SCE was noted at the end of 30 minutes. Impedance experiments were carried out in the frequency range 100 kHz to 0.01 Hz, at the open circuit potential by applying a small amplitude ac signal of 10 mV. The polarization studies were made from -250 mV cathodically to +250 mV anodically versus respective OCP with a scan rate of 1mVs<sup>-1</sup> and the corresponding corrosion currents were recorded.

**Scanning electron microscopy (SEM):** Surface morphology of the mild steel specimen immersed in 0.5 M hydrochloric acid in the absence and presence of optimal concentration of DABBH was recorded by using Scanning electron microscopy EVO 18-5-57 model.

## III. Results and Discussion

**Characterization of DABBH:** Crystalline yellow solid; m. p: 258-260 °C IR (KBr) [cm<sup>-1</sup>]: 1596 (C=N str.), 1620(C=O), 1580 (Ar. C=C str.), 3116.75 (CH str.), 3178 (NH str.), 3471(OH); 2908 (C-H assystr), (2808 C-H symstr).

**Tafel polarization measurement:** Tafel polarization curve for the corrosion of mild steel in different concentrations of DABBH, at 30 °C is shown in Figure 2.



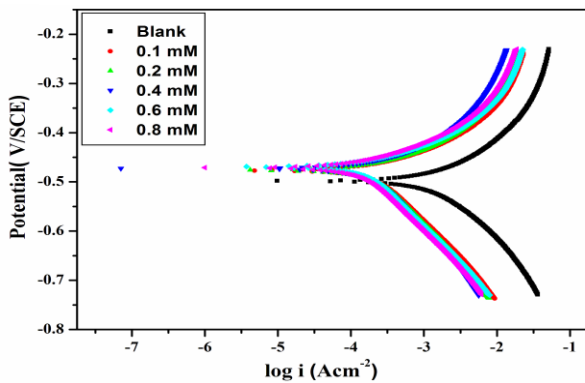


Figure 2. Tafel polarization curves for the mild steel specimen in 0.5 M HCl with various concentrations of DABBH at 30 °C

The corrosion rate (CR) was calculated using equation, [4]

$$CR = \frac{3270 \times E.W \times i_{corr}}{D} \quad (1)$$

Where, 3270 is a constant that defines the unit of corrosion rate,  $i_{corr}$  = corrosion current density in  $A/cm^2$ , D = density of the corroding material ( $7.75 g/cm^3$ ), E.W = equivalent weight of mild steel (27.925).

The percentage inhibition efficiency (% IE) was calculated as

$$\% IE = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \times 100 \quad (2)$$

Where,  $i_{corr}$  and  $i_{corr(inh)}$  are corrosion current densities in the absence and presence of inhibitor, respectively.

TABLE I. Tafel polarization parameters for the corrosion studies on mild steel in 0.5 M HCl

Temp. (°C)	Conc. of DABBH (mM)	$E_{corr}$ (mV/SCE)	$i_{corr}$ (mA $cm^{-2}$ )	CR (mpy)	IE (%)
30	0	-491	1.405	342	
	0.1	-486	0.3410	83.22	75.7
	0.2	-485	0.3304	80.08	76.5
	0.4	-481	0.3160	77.12	77.5
	0.6	-478	0.2789	68.07	80.1
	0.8	-478	0.2117	51.66	84.9
40	0	-489	3.001	732	
	0.1	-486	0.5421	132.3	81.9
	0.2	-482	0.4809	117.4	83.9
	0.4	-484	0.4375	106.8	84.1
	0.6	-485	0.3722	90.82	87.5
	0.8	-484	0.3090	75.42	89.7
50	0	-499	5.887	1437	
	0.1	-494	0.8911	217.5	84.8
	0.2	-490	0.7355	180.0	87.5
	0.4	-492	0.6519	159.1	88.9
	0.6	-497	0.4747	115.8	91.9
	0.8	-500	0.4041	98.61	93.1
60	0	-502	11.35	2771	

	0.1	-502	1.1720	286.0	89.6
	0.2	-499	0.9855	240.2	91.3
	0.4	-485	0.8961	218.7	92.1
	0.6	-503	0.7683	189.5	93.2
	0.8	-505	0.6625	160.2	94.1

The value of corrosion current density (TABLE 1.) decreased effectively even at low concentration of DABBH and inhibition efficiency increases with increase inhibitor concentration. The presence of inhibitor does not shift the  $E_{corr}$  remarkably, implying that DABBH acts as a mixed type inhibitor affecting both anodic and cathodic reactions. According to Li and others [5], if the displacement in corrosion potential is more than  $\pm 85mV$  with respect to corrosion potential of the blank, the inhibitor can be considered as a cathodic or anodic type. But the maximum displacement in the present case is less than 20mV, which indicates that DABBH is a mixed type inhibitor. The anodic and cathodic Tafel slopes remain almost unchanged upon addition of the inhibitor. Thus the adsorbed inhibitor acts by simple blocking of active sites for anodic and cathodic processes, thereby reducing the surface area for corrosion without affecting the corrosion mechanism. The addition of DABBH brings down the corrosion rate to the minimal level and further the inhibition efficiency increases with increase in temperature. This may be due to the fact that physisorption favours at lower temperature, whereas chemisorption at higher temperature [6].

The activation energy ( $E_a$ ) for the corrosion process was calculated from Arrhenius equation, [7]

$$\ln (CR) = B - \frac{E_a}{RT} \quad (3)$$

Where, B is the Arrhenius pre-exponential constant, and R is the universal gas constant. The slope ( $-E_a/R$ ) obtained from the plot of  $\ln (CR)$  against  $1/T$  (Figure 3.) is used to calculate the activation energy. The enthalpy of activation ( $\Delta H^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) for the metal dissolution process are determined using the transition state equation, [8]

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \quad (4)$$

Where, h is Plank's constant and N is Avagadro's number. The plot of  $\ln (CR/T)$  vs  $1/T$ , gives a straight line (Figure 3.)

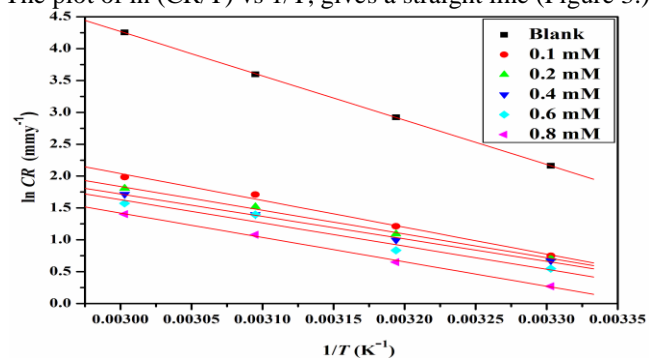


Figure 3. Plot of  $\ln (CR)/T$  versus  $1/T$  for mild steel in 0.5 M HCl containing various concentrations of DABBH



TABLE II. Activation parameters for the corrosion of mild steel in 0.5 M HCl

Conc. of DABBH (mM)	$E_a$ (kJmol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJmol <sup>-1</sup> )	$\Delta S^\ddagger$ (Jmol <sup>-1</sup> K <sup>-1</sup> )
0	57.83	55.20	-75.20
0.1	35.03	32.29	-162.14
0.2	30.99	28.36	-175.94
0.4	29.29	26.66	-182.02
0.6	30.24	27.61	-179.92
0.8	31.81	29.17	-176.07

with slope =  $-\Delta H^\ddagger/T$  and intercept =  $\ln(R/Nh) + \Delta S^\ddagger/R$ . The activation parameters obtained are recorded in Table II. The decrease in activation energy ( $E_a$ ) with increase in inhibitor concentrations indicates that adsorption of inhibitor takes place through chemisorption. The negative value of  $\Delta S^\ddagger$  signifies that an increase in disordering takes place on going from reactant to the activated complex, and positive value of  $\Delta H^\ddagger$  indicate the endothermic nature of steel dissolution process [9].

**Electrochemical impedance spectroscopy (EIS):** EIS measurements were carried out at different temperatures and the corresponding Nyquist plots were recorded (Figure 4.).

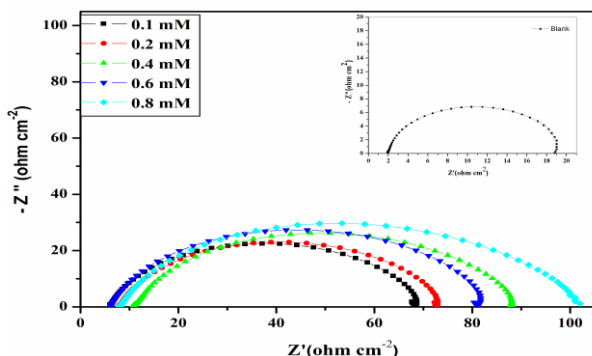


Figure 4. Nyquist plots for mild steel in 0.5 M HCl acid containing different concentrations of DABBH at 30 °C

It is clear from these plots that the impedance response of mild steel in uninhibited acid solution has significantly changed after the addition of inhibitor to the acid medium. This indicates that the impedance of the inhibited substrate has increased with increasing concentration of DABBH. The impedance parameters are analysed by fitting suitable equivalent circuit to the Nyquist plots using ZSimpWin software version 3.21. Figure 5. shows the simple Randles circuit used to fit the impedance data in the absence of inhibitor and presence of inhibitor. It consists of solution resistance ( $R_s$ ), constant phase element (CPE) in parallel with a charge transfer resistance ( $R_{ct}$ ). The CPE was introduced in the circuit instead of pure double layer capacitor ( $C_{dl}$ ) to give more accurate fit. The impedance of CPE can be given by the expression, [10]

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (5)$$

Where  $Y_0$  is the proportionality coefficient,  $\omega$  is the angular frequency,  $j$  is the imaginary number and  $n$  is the exponent related to the phase shift. If the value of  $n=1$ , the CPE behaves like an ideal double layer capacitance ( $C_{dl}$ ). The correction in the capacitance to its real value was calculated using the relation, [11]

$$C_{dl} = Y_0 (W_{max})^{n-1} \quad (6)$$

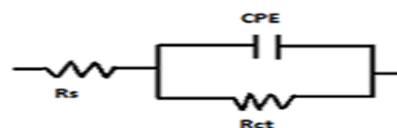


Figure 5. Equivalent circuits used to fit experimental EIS data for the corrosion of mild steel in 0.5 M HCl medium in the absence and presence of DABBH

The charge transfer resistance  $R_{ct}$  is a measure of resistance against electron transfer across the surface and is inversely proportional to corrosion rate. Further, the  $R_{ct}$  values increase with increase in inhibitor concentration, which indicates that the corrosion process is mainly controlled by charge transfer process [12]. The  $R_{ct}$  obtained from the equivalent circuit is used to calculate the percentage inhibition efficiency (% IE).

$$\% IE = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (7)$$

Where,  $R_{ct}$  and  $R_{ct}^0$  indicate the charge transfer resistance in presence and absence of DABBH.

It is observed from the TABLE III. that the values of  $C_{dl}$  decreases with increase in inhibitor concentrations at all studied temperatures. The decrease in  $C_{dl}$  is due to the increase in electrical double layer at the metal solution interface and the gradual replacement of water molecules owing to the adsorption of organic molecules on the metal surface [13] The  $R_{ct}$  values increase with increase in inhibitor concentration, which indicates that the corrosion process is mainly controlled by charge transfer process [14].

TABLE III. EIS results for mild steel in 0.5 M HCl in the absence and presence of DABBH

Temp. (°C)	Conc. of DABBH (mM)	$R_{ct}$ (ohm cm <sup>2</sup> )	$C_{dl}$ (μF cm <sup>2</sup> )	IE (%)
30	0	16.75	1279	
	0.1	62.81	114.5	73.3
	0.2	65.75	107.6	77.8
	0.4	75.52	88.18	78.0
	0.6	78.44	79.59	78.6
40	0.8	94.15	57.09	82.2
	0.1	47.33	116.1	80.0

	0.2	48.29	113.9	80.2
	0.4	50.55	102.2	83.8
	0.6	51.14	90.15	85.0
	0.8	61.87	75.27	86.7
50	0	5.70	10615	
	0.1	34.83	404.9	83.6
	0.2	35.27	374.4	83.8
	0.4	40.52	296.8	85.9
	0.6	45.18	256.3	87.3
	0.8	60.35	178.1	90.5
60	0	2.33	45560	
	0.1	18.18	1268	87.1
	0.2	19.38	1092	87.9
	0.4	25.22	688.1	90.7
	0.6	26.0	659.8	91.0
	0.8	27.15	584.7	91.4

**Adsorption isotherm:** In the present study, various adsorption isotherms are tested and it is found that the adsorption of DABBH on the mild steel surface in 0.5 M hydrochloric acid medium follows the Langmuir adsorption isotherm (Figure 6.) which is governed by the equation, [15]

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (8)$$

Where,  $C_{inh}$  is inhibitor concentration,  $\theta$  is the degree of surface coverage and  $K_{ads}$  is the adsorption equilibrium constant.

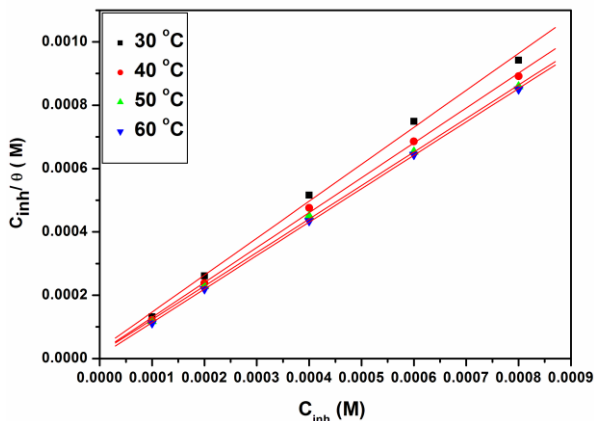


Figure 6. Langmuir's adsorption isotherm of DABBH on mild steel in 0.5 M HCl at different temperatures

The value of  $K_{ads}$ , determined from the plot of  $C_{inh}/\theta$  vs.  $C_{inh}$  (Figure 6.) at constant temperature is used to calculate the value of the standard free energy of adsorption ( $\Delta G_{ads}^{\circ}$ ) using the expression, [16]

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^{\circ}}{RT}\right) \quad (9)$$

Where,  $K_{ads}$  is the equilibrium constant,  $R$  is the universal gas constant and  $T$  is absolute temperature and 55.5 is the concentration of water in solution in  $\text{mol}/\text{dm}^3$ . The plot of  $\Delta G_{ads}^{\circ}$  versus  $T$  gives a straight line (Figure 7.).

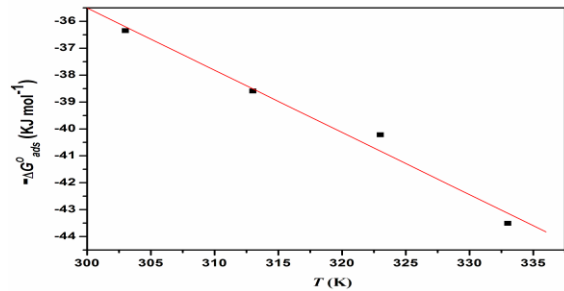


Figure 7. Plot of  $\Delta G_{ads}^{\circ}$  versus temperature for the adsorption of DABBH on mild steel in 0.5 M HCl

The standard enthalpy of adsorption ( $\Delta H_{ads}^{\circ}$ ) and the standard entropy of adsorption ( $\Delta S_{ads}^{\circ}$ ) are computed from the slope and intercept of the straight line respectively according to the thermodynamic equation (10).

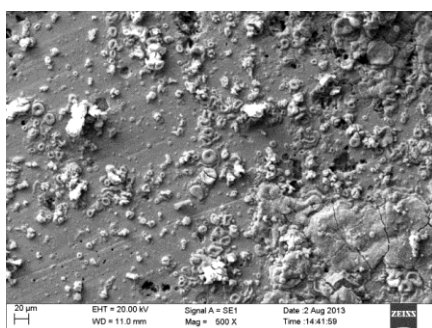
$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T \Delta S_{ads}^{\circ} \quad (10)$$

TABLE IV. Thermodynamic parameters for the adsorption of DABBH on mild steel surface

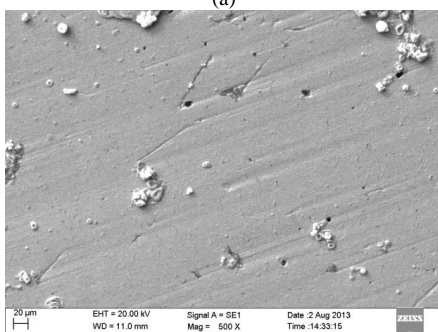
Temp. (°C)	$\Delta G_{ads}^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta H_{ads}^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta S_{ads}^{\circ}$ (Jmol <sup>-1</sup> K <sup>-1</sup> )
30	-36.35	33.82	-231.11
40	-38.59		
50	-40.22		
60	-43.52		

In general, the values of  $\Delta G_{ads}^{\circ}$  up to  $-20 \text{ kJ mol}^{-1}$  or less than  $-20 \text{ kJ mol}^{-1}$  imply the formation of electrostatic interactions between the charged molecules and the charged metal surface. The values greater than  $-40 \text{ kJ mol}^{-1}$  imply the formation of the chemical bond between the inhibitor molecule and the metal surface through charge sharing or charge transfer [17]. In this case  $\Delta G_{ads}^{\circ}$  values corresponding to lower temperature (30 and 40°C) indicates the mixed adsorption of DABBH, predominately with chemisorption at higher temperatures. In general, an endothermic process is attributed to chemisorption while an exothermic adsorption process signifies either physisorption or chemisorption. In the present study, the calculated value of  $\Delta H_{ads}^{\circ}$  with positive sign indicates the chemisorption of inhibitor. The large and negative  $\Delta S_{ads}^{\circ}$  value indicates that an increase in disorder takes place on going from reactant to the metal activated complex [18].

**Scanning electron microscopy:** The surface images of mild steel sample in the absence and presence of DABBH are shown in Figure 8.(a) & 8.(b) respectively. The Figure 8. (a) shows the formation of rough surface including pits due to the corrosion, whereas smooth sample surface was obtained in the presence of DABBH as shown in Figure 8. (b). This confirms the adsorption of DABBH on the mild steel surface through the formation of protective film.



(a)



(b)

Figure 8. SEM images of the mild steel in (a) 0.5 M HCl solution and (b) 0.5 M HCl containing 0.8 mM of DABBH

## IV. Conclusion

DABBH acts as an efficient mixed type inhibitor and its inhibition efficiency increases with the increase in inhibitor concentration and increase in temperature. Activation and thermodynamic parameters indicate that the adsorption of DABBH takes place predominantly through chemisorption with mixed adsorption at lower temperature (40 & 50°C) and follows Langmuir's adsorption isotherm.

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N'-[4-(dimethylamino)benzylidene]-4-hydroxybenzoic acid acts as a potential mixed type corrosion inhibitor for mild steel in 1 M HCl medium.