

Corrosion Inhibition, Adsorption behaviour and Thermokinetic Characteristics of 1-Benzyl-3-Hydroxy-1-H-Indazole on Mildsteel in Neutral Medium

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ABSTRACT: The influence of an aromatic indazole derivative 1-Benzyl-3-Hydroxy-1-H-Indazole (BHI) as corrosion inhibitor on mildsteel in 60ppm Cl⁻ ion was studied by weight loss method and temperature studies ranging from 303K-343K. The results showed that Inhibition efficiency of BHI increase with increasing inhibitor concentration and decreased with increasing temperature. The neutral medium was found fit well for future studies. Furthermore, temperature parameter of adsorption process such as activation energy(E_a), ΔH , ΔS , K_{ads} were calculated and these value showed a good interaction. The adsorption of BHI on carbon steel surface is endothermic, spontaneous and consistent with langmiur, Freundlich, Temkin adsorption isotherms. Surface characterization using FT-IR, scanning electron microscopy(SEM) and Energy dispersive x-ray spectroscopy(EDS) is used to ascertain nature of protective film. The mechanistic aspects of corrosion inhibition are proposed.

KEYWORDS: Corrosion, Mildsteel, SEM, EDS, Adsorption isotherms.

I.INTRODUCTION

Mildsteel is widely applied as construction material in many chemical and petrochemical industries due to its excellent mechanical properties and low cost. Corrosion in cooling water system greatly affects the health of human beings and economical level of world[1]. One of most practical methods for protection against excessive dissolution of mildsteel by corrosion is the use of proper inhibitor[2]. To reduce the corrosion problem in these environments inhibitive effects of organic compounds have been tried[3]. They reduce the corrosion rate by either acting as barrier or by forming an adsorbed layer or retarding the cathodic and/or anodic process[4]. There are various organic inhibitor which tend to decreasing the corrosion rate of mildsteel. Most of the effective organic inhibitor used, contain hetero atom such as O, N, S and multiple bonds in their molecules through which they are adsorbed on metal surface[5]. It has observed that adsorption depends mainly on certain physiochemical properties of the inhibitor group, such as electron density at the donor atom, π -orbital character, and the electronic structure of the molecule[6]. Most of corrosion inhibitor possess an active functional group such as nitro(NO_2) or hydroxyl group[7,8].

In the present work the inhibitive effect of using a new organic inhibitor viz., BHI and Zn^{2+} ion in controlling the corrosion of the mildsteel in neutral aqueous environment containing low chloride has been studied by non-electrochemical studies (weight loss, temperature studies, various immersion time). Surface analytical techniques viz., FT-IR, SEM, EDS were used to study the nature of protective film formed on the metal surface.

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II. REVIEW OF LITERATURE

M.A.Quraishi and F.A.Ansari[2006], have investigated the inhibition efficiency of organic inhibitors. Q.B.Zhang and Y.X.Hua(2009). have studied the corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. Schweifzer,P.A(2007) has analysed Corrosion of linings and coating of cathodic and inhibition protection and corrosion monitoring of mild steel. A.S.Fouda and A.HamdyBadr(2013) have determined IE of aqueous extract of propolis as corrosion inhibitor for carbon steel in aqueous solution. I.B.Obot,(2009) have studied, the antifungal drugs as corrosion inhibitors for aluminium in 0.1M HCl.

III. EXPERIMENTAL

2.1 Material preparation

Mild steel specimen of same sheet having composition 0.1% C, 0.026% S, 0.06% P, 0.04%Mn,rest iron and the dimensions of 1.0 X 4.0 X 0.2 cm. The carbon steel specimens were mechanically abraded, degreased, rinsed dried and weighed before immersion in the experimental solution. Chemicals and reagents used were Analar/ Sigma Aldrich grade.

2.2 Weight loss measurements

Weight loss measurements were carried out in triplicate in absence and presence of BHI for various concentrations, pH and immersion time in 60ppm Cl⁻ ions in the temperature range 303K-343K.

2.3 Surface analysis

FT-IR : FT-IR were recorded with the frequency ranging from 4000-400 cm⁻¹.For FT-IR studies, analytical SHIMADZU MIRacle 10 instrument was used. **SEM**:The polished mildsteel specimens were immersed in blank and inhibitor solution for 3 hours, washed, dried and SEM photographs were investigated using ZEISS model. **Energy Dispersive Analysis of X-Ray Spectroscopy**: EDS system attached with a ZEISS Scanning Electron microscope was used for elemental analysis before and after applying the inhibitor.

IV. RESULTS AND DISCUSSION

3.1 Weight loss measurements

The optimum best concentration of 120 ppm for the inhibitor system is evaluated by weight loss measurements and 61.4% is obtained for 3 hours for immersion period. In neutral media maximum efficiency is achieved.

Table 1: Effect of immersion time on IE of blank and inhibitor system

Conc (ppm) BHI	1 hr		3 hr		5 hr		9 hr		12 hr		24 hr	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
0 (blank)	-	0.2231	-	0.2604	-	0.2678	-	0.2728	-	0.2790	-	0.3347
120	50	0.3347	61.4	0.1004	60.4	0.1059	59.1	0.1116	50	0.1395	48.6	0.1831

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The optimum concentration inhibitor system shows the decrease in IE with immersion period as shown in Table 1 and Fig.1(a). It is due to desorption of inhibitor molecules from the metallic surface with time and instability of inhibitive complex on MS surface.

Table 2: Effect of pH on IE and CR of blank and inhibitor system

System	Acidic				Neutral	Basic			
	pH 0	pH 1	pH 3	pH 5	pH 7	pH 8	pH 10	pH 12	pH 14
Cl ⁻ ion (60 ppm) CR (mmpy)	3.831	3.682	2.901	1.450	0.2604	3.161	2.715	2.306	1.971
Cl ⁻ ion (60 ppm) + BHI (200 ppm) +Zn ²⁺ (90 ppm) CR (mmpy)	3.049	2.083	1.302	0.5211	0.0744	1.078	0.9669	1.2645	1.4132
IE (%)	20.4	43.4	55.1	64	71.4	65.8	64	45.1	28.3

Further inhibition efficiency is found to decrease in acidic and basic media, as given in Table 2 and Fig.1b. In acidic media aggressive chloride ions cause more corrosion and in basic media hydroxyl ions remain in bulk of the solution and not able to transport inhibitor molecules onto metal surface with the help of carrier molecules of Zn(OH)₂.

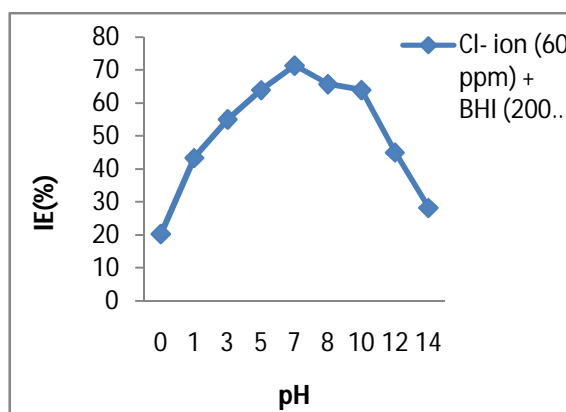
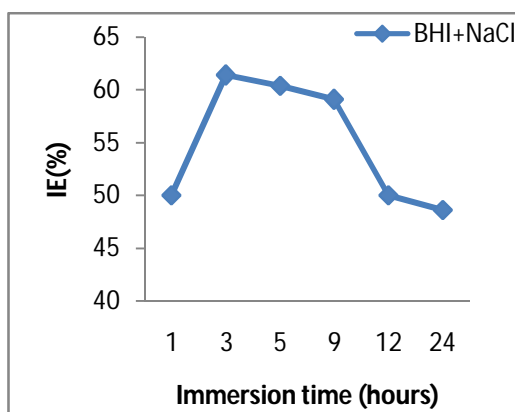


Figure 1(a): Effect of immersion time on IE ,

(b): Effect of pH on IE of inhibitor system

3.2 Effect of temperature

The effect of temperature on the IE of inhibitor by weight loss method at different concentrations and at different temperatures (303K-343K) shown in Table 3 and Figure 2 Table 3:Effect of Temperature on IE and CR

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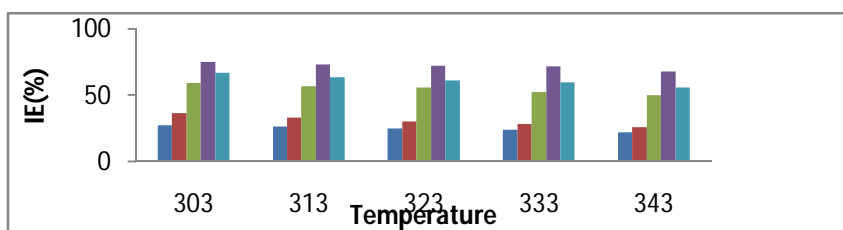
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BHI	303 k		313 k		323 k		333 k		343 k	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
0	-	0.4090	-	0.5579	-	0.6694	-	0.7810	-	0.9298
20	27.3	0.2975	26.6	0.4091	25	0.5021	23.8	0.5950	22	0.7252
60	36.4	0.2603	33.3	0.3719	30.5	0.4648	28.6	0.5578	26	0.6880
100	59.1	0.1619	56.7	0.2417	55.6	0.2975	52.4	0.3719	50	0.4649
120	75	0.1116	73.3	0.0517	72.2	0.1859	71.4	0.2231	68	0.6694
140	66.6	0.1488	63.3	0.2045	61.1	0.2603	59.5	0.3161	56	0.4091

It is revealed that inhibition efficiency decreased by increasing temperature, due to desorption of adsorbed inhibitor components on carbon steel surface. This indicates that the inhibitor system of various concentrations are physically adsorbed on metal surface [9].

Figure2: Variation of IE(%) at different temperature



3.3 Thermodynamic Parameters

The apparent activation energy E_a of metal corrosion in aqueous medium in presence and absence of inhibitor were calculated from Arrhenius equation and presented in Table 4.

$$CR = K \exp(-E_a/RT)$$

CR corrosion rate, R universal gas constant, K pre-exponential constant E_a activation energy and T absolute temperature. Figure 3 represents the Arrhenius plot of $\log CR$ Vs $1/T$ for uninhibited and inhibited solutions. The E_a values from Table 4 calculated from the slopes of the Arrhenius plot is higher in the presence of inhibitor (41.95 kJ/mol) compared to blank (16.45kJ/mol).

The higher value of activation energy in the presence of inhibitor than in its absence is attributed to its physical adsorption and its chemisorptions [10] while pronounced in the opposite case [11]. In the presence study the higher value of E_a for mildsteel in an inhibitor's presence, compared to that in its absence, indicates the formation of physisorbed monolayer. An alternative form of Arrhenius equation is the transition state equation

$$CR = (RT/Nh) \exp(\Delta S^*/R) \exp(\Delta H^*/RT)$$

Where 'h' is Planck's constant, N Avogadro's number, ΔS^* entropy of activation, ΔH^* enthalpy of activation. A plot of $\log CR/T$ Vs $1/T$ gave a straight line (Fig. 3) with the slope of $(-\Delta H^*/2.303RT)$ and an intercept of $[\log(R/Nh) + (\Delta S^*/R)]$, from which the values of ΔH and ΔS were calculated and listed in table 4.

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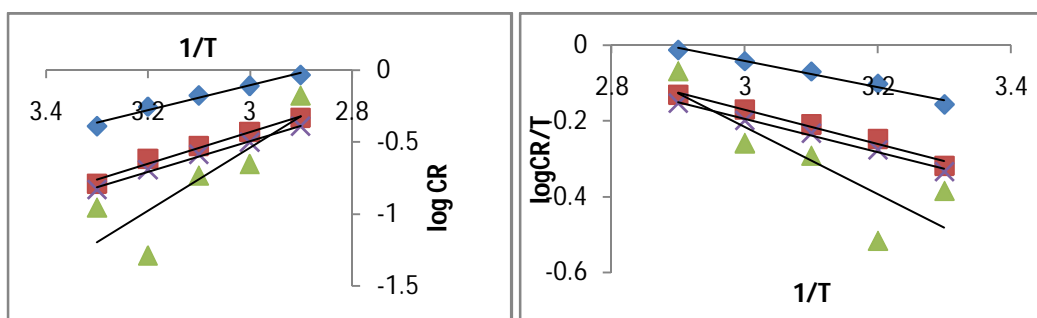
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Table 4: Activation Parameters

Inhibitor concentration (ppm)	Ea (kJ / mol)	ΔH_a (kJ / mol)	ΔS_a J/mol/K
0	16.45	16.42	-150
100	21.12	21.17	-142.3
120	41.95	41.92	-82.04
140	20.44	20.41	-145.62

Figure 3: Calculation of activation energy plot of log CR Vs 1/T and log CR/T Vs 1/T



The positive values of ΔH for corrosion of mildsteel in the presence and absence of inhibitor reflect the endothermic nature of metal dissolution process. The negative value of ΔS reveals decrease in randomness on going from reactant to activated complex [12]. This reflects the formation of ordered stable film of inhibitor on mildsteel surface.

3.4 Adsorption Isotherms

Adsorption isotherm values are important to explain the corrosion inhibition of organo electrochemical reactions. The metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore the adsorption of inhibitor molecules from aqueous solution is a quasi substitution process. The weight loss temperature results were used to calculate the adsorption isotherm parameters. Many adsorption isotherms were plotted and Langmuir, Temkin and Freundlich was found to be better description of the adsorption behavior. The experimental data were tested graphically to fit a Langmuir, Temkin, Freundlich isotherms. For all isotherms the linear regression parameters are listed and tabulated in 5 and plotted in Figure 4. The regression coefficients for Langmuir, Temkin and Freundlich were found closer to unity. The adsorption leads to high degree of surface coverage and better inhibitive property.

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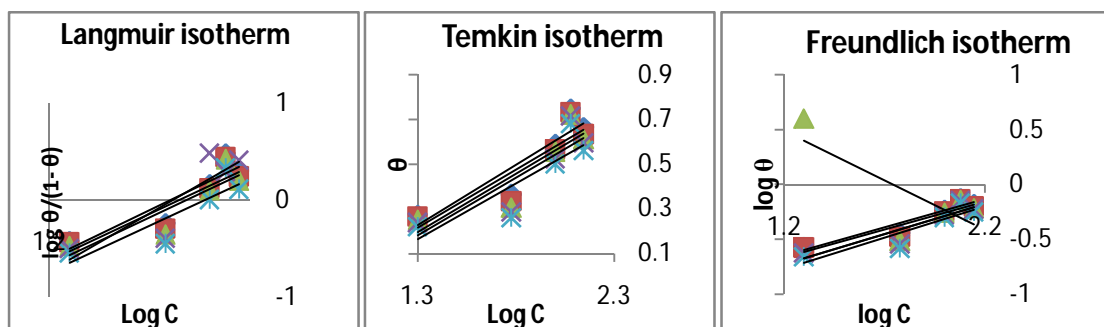
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Table 5: Adsorption Parameters

Inhibitor system	Adsorption isotherm		
	Langmuir	Temkin	Freundlich
	R ²	R ²	R ²
303	0.83	0.83	0.90
313	0.80	0.80	0.86
323	0.78	0.77	0.84
333	0.77	0.75	0.82
343	0.76	0.74	0.81

Figure 4: Adsorption Isotherm



3.5 Thermodynamic parameters of adsorption of inhibitor system in aqueous medium

Thermodynamic parameters play an important role in understanding the inhibitive mechanism. ΔG^0_{ads} was calculated using the equation

$$\Delta G^0_{ads} = -RT \ln (55.5 XK_{ads})$$

Where K adsorption equilibrium constant, R gas constant (8.314 J/K/Mol), T absolute temperature in Kelvin and 55.5 is the concentration of water in solution expressed in mol/Lt [13]. The free energy of adsorption is related to the equilibrium constant of adsorption using the following equation " $K_{ads} = 1/55.5 \exp(\Delta G^0_{ads})/RT$ "

The negative values of ΔG^0_{ads} given in Table 6 indicate the stability of the adsorbed layer on mildsteel surface and spontaneity of the adsorption process. In present work the calculated values $-8.79 \leq \Delta G^0_{ads} \leq -14.65$ kJ/mol, less than threshold value (-40kJ/mol) required for chemical adsorption and the IE (%) decreased with increased temperature, support mechanism of physical adsorption. Enthalpy (ΔH^0_{ads} kJ/mol) and entropy (ΔS^0_{ads} kJ/mol) of adsorption can be calculated from rearranged Gibbs Helmholtz equation. $\Delta G^0 = \Delta H^0_{ads} - \Delta S^0_{ads} T$. Figure 5 shows dependence of ΔG^0_{ads} on T indicating an appropriate relationship between thermodynamic parameter. The calculated values are listed in Table 6. The positive values of ΔH^0_{ads} (10.77 – 16.68kJ/mol) reveals adsorption is an endothermic process and suggesting physisorption. Generally enthalpy values are less than or around the 40 kJ/mol, the adsorption process is physisorption while in the case of the value more than 100 kJ/mol, the adsorption of inhibitor follow chemisorptions process [14]. The ΔS^0_{ads} values deviating from negative to more positive side (-0.007 to 0.014) indicates the randomness at the metal solution interface.

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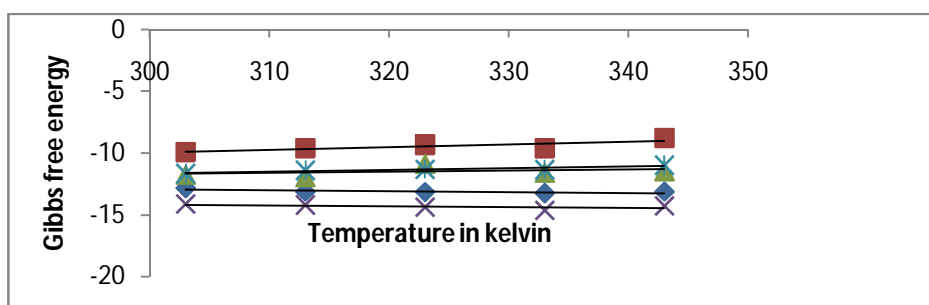
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Table 6: Thermodynamic parameters

Conc. (ppm)	ΔG^0_{ads} (kJ/mol)					ΔS^0_{ads} (kJ/mol)	ΔH^0_{ads} (J/mol/K)
	303 K	313K	323K	333K	343K		
20	-12.86	-13.148	-13.178	-13.27	-13.163	-0.07	10.77
60	-9.91	-9.61	-9.321	-9.61	-8.79	0.022	16.68
100	-11.73	-11.93	-10.87	-11.58	11.45	0.009	14.45
120	-14.14	-14.21	-14.41	-14.65	-14.29	-0.007	11.95
140	-11.67	-11.4	-11.325	-11.35	-10.98	0.014	15.96

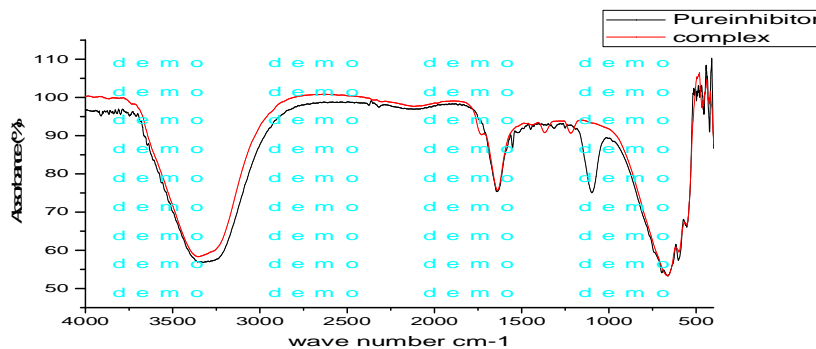
Figure 5: Plot of various Temperatures Vs ΔG^0_{ads}



3.6 Spectroscopic Techniques:

FT-IR spectroscopy investigate the nature and center of adsorption to confirm the inhibitive film formation on mildsteel surface. It is observed, some of peaks have either disappeared or shifted indicating complex formation as a pre-requisite condition for inhibitive formation. The FT-IR spectrum of BHI-Zn²⁺ (20ppm) aqueous medium containing 60ppm Cl⁻ ion is shown in figure 6

The OH stretching frequency has been shifted from 3352 cm⁻¹ to 3326 cm⁻¹ and N-H stretching shifted from 3352 cm⁻¹ to 3355 cm⁻¹. similarly N=N peak shifted from 1638 cm⁻¹ to 1640 cm⁻¹ and C=C stretching frequency shifted from 1637 cm⁻¹ to 1643 cm⁻¹. The peak at 1637 cm⁻¹-1643 cm⁻¹. The peak at 1637 cm⁻¹ is due to Zn(OH)₂[15].0



The FT-IR Suggests that the protective film may consists of [Fe²⁺/Zn²⁺-BHI], Zn(OH)₂ and considerably less amount of oxides and hydroxides of Iron.

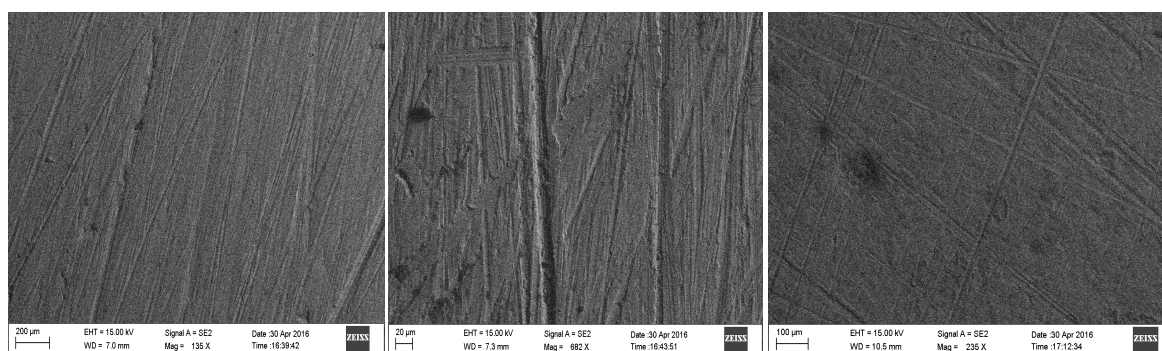
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3.7 Scanning Electron Microscopy

Figure 13- SEM images of (a) polished metal (b) 60 ppm Cl⁻ ion (c) 60 ppm Cl⁻ ion+20 ppm Zn²⁺ ion + 120 ppm BHI



7(a)

7(b)

7 (c)

SEM micrograph for polished mildsteel and the mildsteel in the absence and presence of inhibitor. The SEM micrograph of the mildsteel after exposure for 3 hours in a solution without inhibitor is shown in Figure 7(b), has several cracks than the polished metal surface. The cracks in the image show that the metal was corroded severely and contain iron oxides as corrosion product. It can be seen that the adsorbed film is formed and consequently retards the dissolution of metal as shown in Figure 7(c). It may be concluded the SEM micrograph reveals that the surface film formed by the inhibitor system exhibits good inhibitive properties for the mildsteel in aqueous environment.

3.8 Energy Dispersive Analysis of X-Ray Spectroscopy (EDS)

EDS survey spectra were used to determine the composition of elements present in the mildsteel surface before and after exposure to inhibitor solution. The spectrum in case of mildsteel immersed in blank, inhibitor are shown in Figure 8(b), (c). The EDS analysis of mildsteel surface in chloride solution alone showed mainly Fe with small percentages of C, Na, O, Cl, Si which shows corrosion of iron takesplace through the formation of ironoxide or ironchlorides. Low content of chlorine in the EDS Figure 8(c) conforms inhibitor molecule precludes corrosion of through its strong adsorption on mildsteel surface blocking its weak flaws and preventing formation of ferrous and ferric chloride compounds. Therefore, the EDS and SEM examination of mildsteel surface showsformation of protective film on mild steel.

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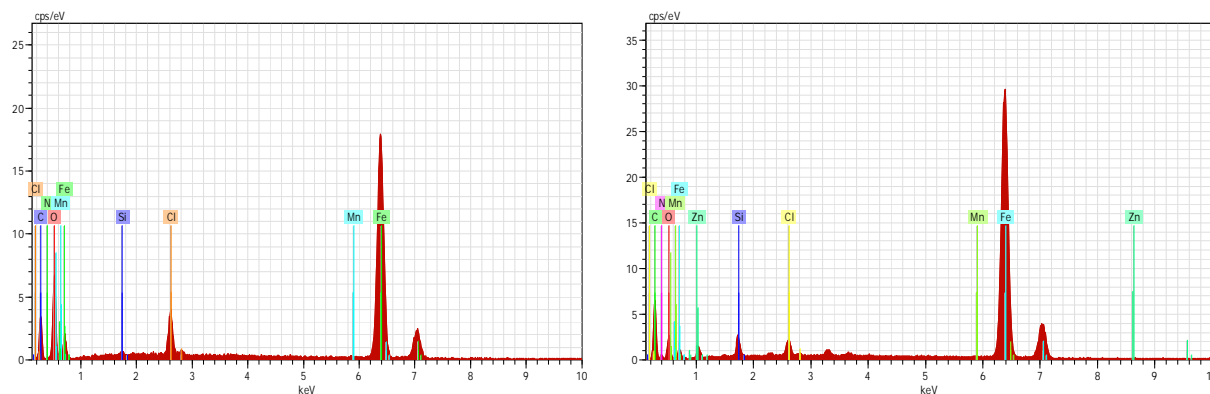
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Table 7: Elemental Composition

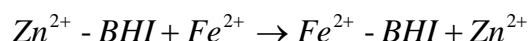
Inhibitor system	Element	Weight	Atomic Weight
Blank (60ppm Cl ⁻ ion)	Fe	34.07	11.66
	C	27.12	43.14
	O	34.49	41.19
	N	2.02	2.75
	Si	0.16	0.11
	Cl	2.14	1.15
60ppmCl ⁻ ion+120ppmBHI+20ppm Zn ²⁺	Fe	42.90	15.14
	C	36.22	59.42
	O	13.09	16.13
	N	5.68	7.99
	Si	1.24	0.87
	Cl	0.76	0.42
	Zn	0.19	0.03

Figure 8: EDS of (a) Blank, (b) inhibitor system



IV. CONCLUSION

Weight loss studies and thermodynamical studies reveals that the formulation consisting of 120ppmBHI+20ppmZn²⁺+60ppm Cl⁻ ion offers best efficiency to carbon steel immersed in 60ppmCl⁻ neutral aqueous medium. The adsorption of BHI on carbon steel follows Langmuir, Freundlich and Temkin isotherm. The Gibbs free energy, Enthalpy and entropy of adsorption indicate adsorption processes spontaneous, endothermic and physical adsorption. FT-IR, EDS&SEM results were in good agreement with the film formation concept on the mildsteel by addition of inhibitor system. The probable mechanism of inhibition attributes formation of complex between the inhibitor and mild steel



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