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# Corrosion inhibition, Adsorption Behaviour and Thermokinetic Characteristics of 1-Benzyl-3-Hydroxy-1-H-Indazole on Mildsteel in Neutral Medium

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

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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(Ea),ΔH, ΔS, Kads 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.*

**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 todecreasing 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 donoratom,$\pi$ $\pi$-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 investigate the nature of protective film formed on the metal surface.

**2.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 carriedout in triplicate in absence and presence of BHI for various concentrations, pH and immersion time in 60ppm $Cl^-$ ions at 303-343K.

**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.

**3. 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. Further inhibition efficiency is found to decrease in acidic and basic media,an increase in immersion period and increase in concentration beyond 120 ppm of inhibitor concentration as shown in Table 1,2..

**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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**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 |

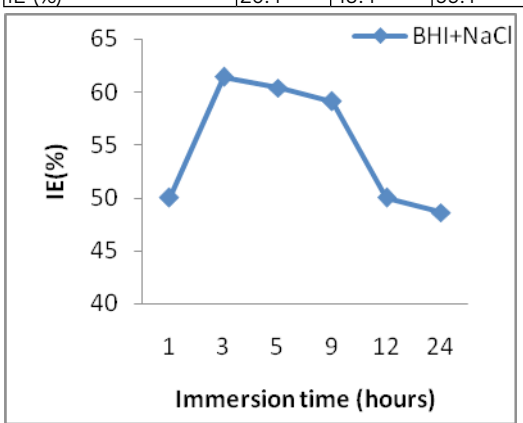



**Figure 1(a): Effect of immersion time on IE ,**

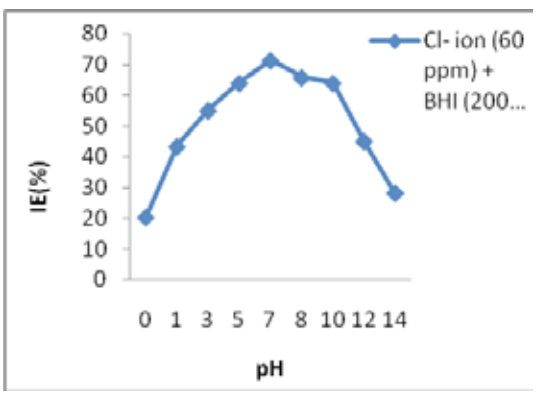



**Figure 1(b): Effect of pH on IE of inhibitor system**

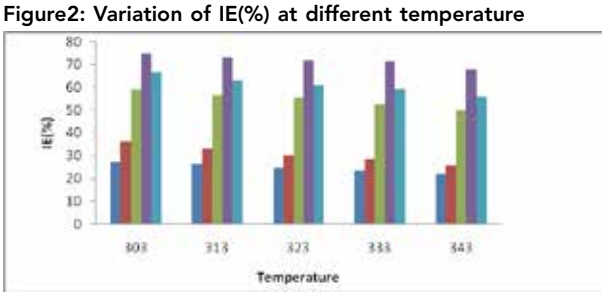
### 3.2 Effect of temperature

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

**Table 3:Effect of Temperature on IE and CR**

| 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 |

**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.

$$CR = Kexp\ (-Ea/RT)$$

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 plots 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

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

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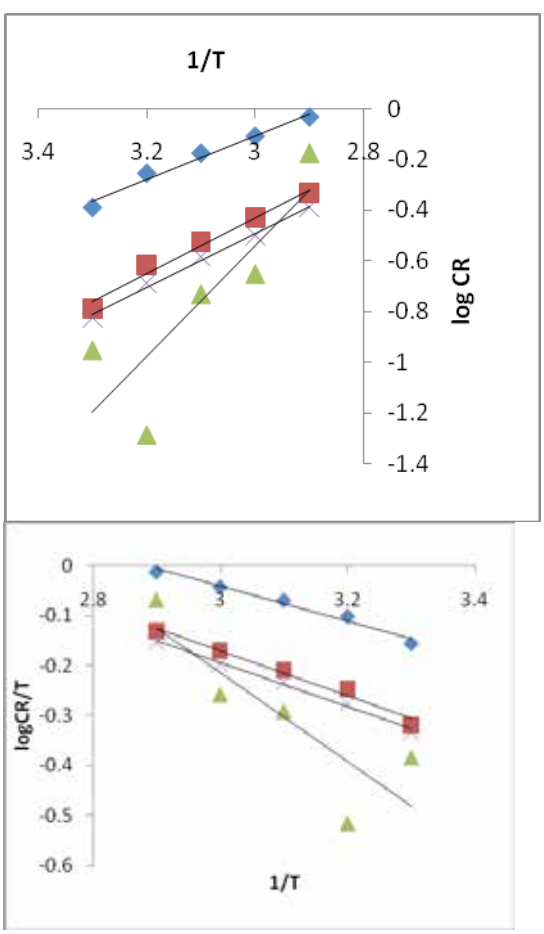
Where 'h' is Planck's constant, N Avogadro's number, $\Delta S^*$ entropy of activation, $\Delta H^*$ enthalpy of activation. A plot of log CR/T Vs 1/T gave a straight line (Fig. 3) with the slope of $(-\Delta H^*/2.303RT)$ and an intercept of $[\log (R/Nh)+(\Delta S^*/R)]$, from which the values of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

**Table 4: Activation Parameters**

| Inhibitor concentration (ppm) | $E_a$ (kJ / mol) | $\Delta H_a$ (kJ / mol) | $\Delta S_a$ 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**




### 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 iostherms the linear regression parameters are listed and tabulated in 5 and plotted in Figure 4.

Langmuir adsorption isotherm

log (θ/1-θ) Vs log C

Temkin adsorption isotherm

θ Vs log C

Freundlich adsorption isotherm

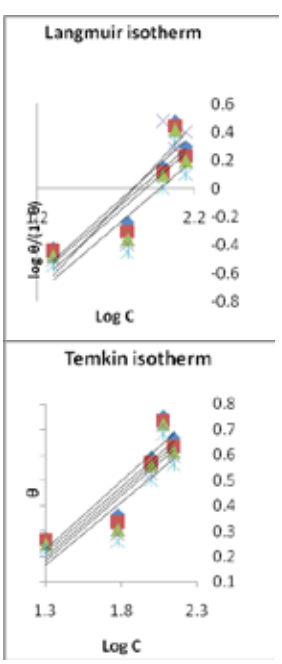
log θ Vs log C

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.

**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**



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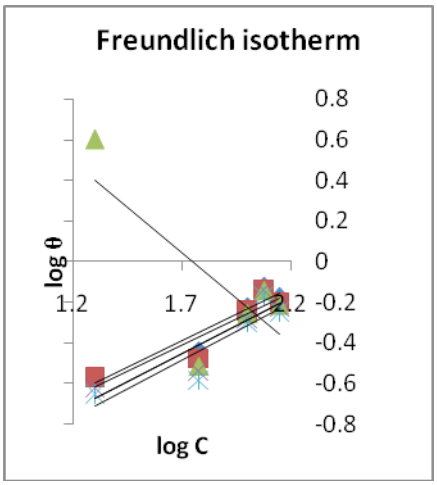



**3.5Thermodynamic parameters of adsorption of inhibitor system in aqueous medium**

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

$$\Delta G^{U}_{ads} = -RTln\,(55.5\,XK_{ads})$$

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

$$K_{ads} = 1/55.5\,exp(\Delta G^{U}_{ads})/RT$$

The negative values of $\Delta G^0_{ads}$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 ≤ $\Delta G^0_{ads}$ ≤ -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 ($\Delta H^0_{ads}$ kJ/mol) and entropy( $\Delta S^0_{ads}$ kJ/mol ) of adsorption can be calculated from rearranged Gibbs Helmholtz equation.

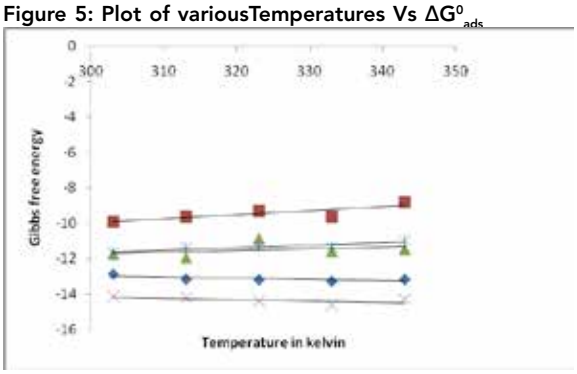
$$\Delta G^{U} = \Delta H^{U}_{ads} - \Delta S^{U}_{ads}$$

Figure 5 shows dependence of $\Delta G^0_{ads}$ on T indicating an appropriate relationship between thermodynamic parameter. The calculated values are listed in Table 6. The positive values of $\Delta H^0_{ads}$ (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 $\Delta S^0_{ads}$ values deviating from negative to more positive side (-0.007 to 0.014) indicates the randomness at the metal solution interface.

**Table 6:Thermodynamic parameters**

| Conc. (ppm) | $\Delta G^0_{ads}$(kJ/mol) | | | | | $\Delta S^0_{ads}$ (kJ/mol) | $\Delta H^0_{ads}$ (J/mol/K) |
|---|---|---|---|---|---|---|---|
| | 303 K | 313K | 323K | 333K | 343K | | |
| 20 | -12.86 | | | | | -0.07 | 10.77 |
| 60 | -9.91 | -9.61 | | -9.61 | -8.79 | 0.022 | 16.68 |
| 100 | -11.73 | -11.93 | | | 11.45 | 0.009 | 14.45 |
| 120 | -14.14 | -14.21 | | | -14.29 | -0.007 | 11.95 |
| 140 | -11.67 | -11.4 | | | -10.98 | 0.014 | 15.96 |

**Figure 5: Plot of variousTemperatures Vs $\Delta G^0_{ads}$**



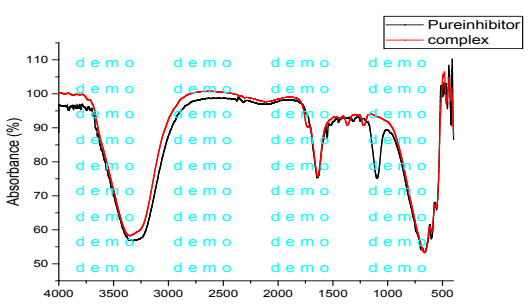

**3.6 Spectroscopic Techniques:**

FT-IR spectroscopyinvestigate the nature and center of adsorption to confirm the inhibitive film formation on mildsteel surface.It is observed, some of peaks have either disappearedor shifted indicating complex formationas a pre-requisite condition for inhibitive formation.

The FT-IR spectrum of BHI-$Zn^{2+}$ (20ppm) aqueous medium containing 60ppm $Cl^-$ ion is shown in figure 6

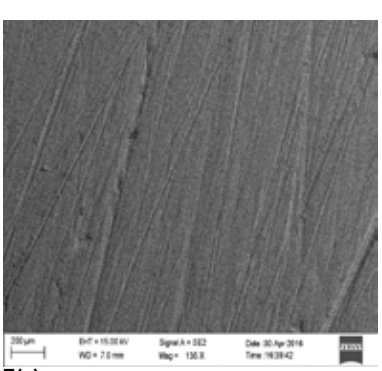
The OH stretching frequency has been shifted from 3352 $cm^{-1}$ to 3326 $cm^{-1}$ and N-H stretching shifted from 3352 $cm^{-1}$ to 3355 $cm^{-1}$.similarly N= N peak shifted from 1638 $cm^{-1}$ to1640 $cm^{-1}$ and C=C stretching frequency shifted from 1637 $cm^{-1}$ to1643 $cm^{-1}$. The peak at 1637 $cm^{-1}$-1643 $cm^{-1}$. The peak at 1637 $cm^{-1}$ is due to$Zn(OH)_2$[15].

The FT-IR Suggests that the protective film may consists of [$Fe^{2+}$/$Zn^{2+}$-BHI],$Zn(OH)_2$ and considerably less amount of oxides and hydroxides of Iron.




**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 $Zn^{2+}$ ion + 120 ppm BHI**



**7(a)**

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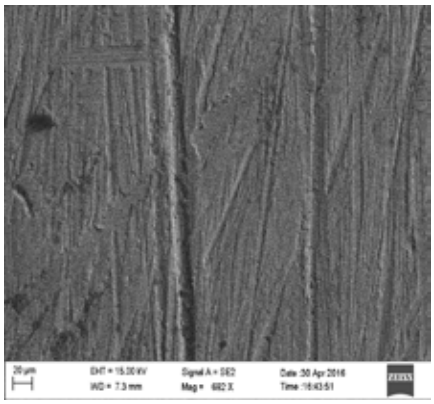
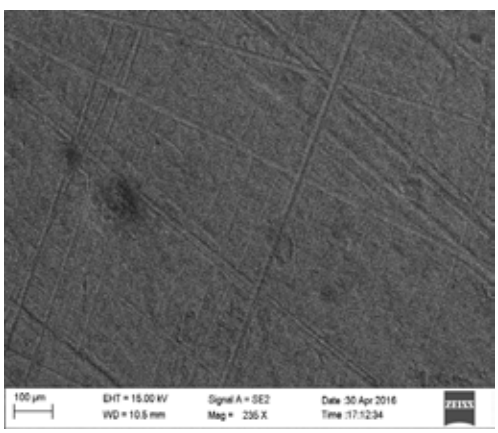


7(b)



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.

**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 |
| 60ppm$Cl^-$ | 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 |

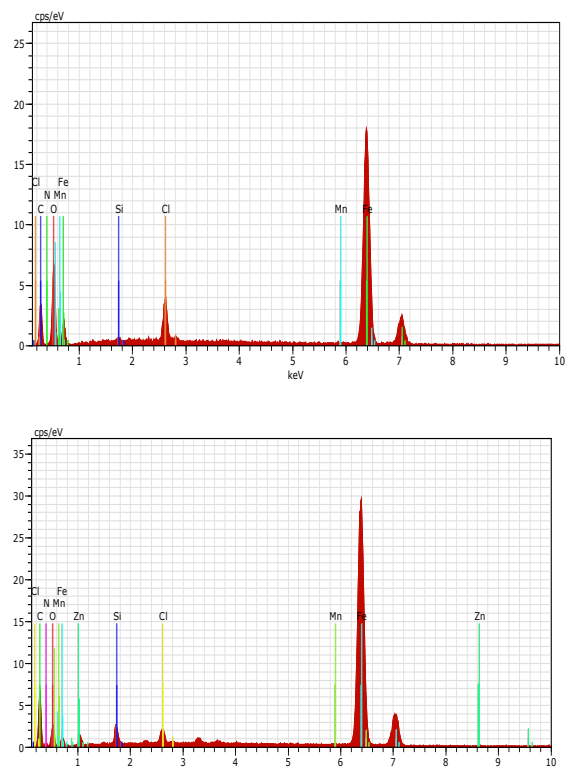



**Figure 8: EDS of (a) Blank, (b) inhibitor system**

### 4. Conclusion

Weight loss studies and thermodynamical studies reveals that the formulation consisting of 120ppmBHI+20ppm$Zn^{2+}$+60ppm $Cl^-$ion offers best efficiency to carbon steel immersed in 60ppm$cl^-$ 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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$$Zn^{2+} - BHI + Fe^{2+} \rightarrow Fe^{2+} - BHI + Zn^{2+}$$

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