

# **Inhibitive Action of Diethyl-4-Methyl-Benzyl Phosphonate (DMBP) On Corrosion of Mild Steel in Aqueous Medium**

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**ABSTRACT:** Corrosion inhibition of mild steel in aqueous solution containing 60 ppm Cl<sup>-</sup> ion by Diethyl-4-Methyl Benzyl Phosphonate with Zn<sup>2+</sup> ion has been studied by weight loss techniques at temperatures ranging from 303 to 343K. It is observed that the proposed organic compound exhibit 71% inhibition efficiency at ambient temperature. Increase in concentration of DMBP inhibition efficiency increases whereas increase in temperature, immersion period decreases inhibition efficiency. The inhibitor show maximum inhibition efficiency for 200 ppm concentration with 90 ppm Zn<sup>2+</sup> at 298K temperature. Activation energy ( $E_a$ ), enthalpy ( $\Delta H_{ads}$ ), entropy ( $\Delta S_{ads}$ ) and Gibbs free energy ( $\Delta G_{ads}$ ) have also been reported. The Langmuir isotherm was found to accurately describe the adsorption behavior of the compound. Electrochemical analysis is carried out to analyze the nature of inhibitor and its action on mild steel. SEM images and FTIR spectra surface studies have used to confirm the nature of inhibitive film .

**KEYWORDS:** corrosion inhibitor, mild steel, thermodynamic parameters, adsorption isotherm, SEM, FTIR.

## **I .INTRODUCTION**

Carbon and low alloy steels are the major construction materials extensively employed in industrial cooling water systems [1] pipe lines and other industrial water distribution systems. However these iron based alloys are inevitably subject to corrosion in neutral or acidic solutions containing aggressive anions [2]. The use of organic molecules as corrosion inhibitors is one of the most popular, efficient and practical method applied to protect metal against corrosion damage [3]. Phosphonate based formulations are well known for corrosion inhibition of carbon steel [4,5] and the impact of phosphonic acid on environment was reported to be negligible at the concentration levels used for corrosion inhibition [6]. Phosphonic acids show synergistic effect with zinc ions and form complexes [7]. In this investigation for the first time the scale inhibition performance of DMBP was studied using different electrochemical , non electrochemical , surface analysis and kinetic and thermodynamic parameter study. Also we evaluated the synergistic influence of Zn<sup>2+</sup> ion on the ability of DMBP in aqueous media.

## **II. MATERIALS AND METHODS**

### **PREPARATION OF MILD STEEL SPECIMENS**

Mild steel specimens were chosen from the same sheet of the following composition 0.1% C, 0.026 % S, 0.06 % P, 0.4% Mn and the rest Iron and the dimensions of 1.0 x 4.0 x 0.2 cm. Prior to all measurements, the carbon steel specimens were mechanically abraded [8] with different types of emery papers (Grade 320 – 400- 600-800-1000-1200), degreased with acetone rinsed with distilled water, dried and weighed before immersion in the experimental solution. These specimens were used for gravimetric measurements. All the chemicals and reagents used were of Analar /Sigma Aldrich Grade

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### Weight loss measurements:

Carbon steel specimens in triplicate were immersed in 100 ml of solutions containing various concentrations of the inhibitor in the presence and absence of  $Zn^{2+}$  for three hours. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution [9]. The inhibition efficiency (IE) was then calculated using the equation.

$$\text{Efficiency of Inhibitors (\%)} = \frac{WL_w - WL_i}{WL_w} \times 100$$

Where  $WL_w$  is the weight loss without inhibitor and  $WL_i$  is the weight loss with inhibitor.

ADSORPTION ISOTHERMS: various isotherms [10] like Langmuir, Temkin, Frumkin, and Freundlich are studied.

SURFACE EXAMINATION STUDIES by FTIR, SEM [11] analysis are carried out to study surface morphology of inhibited and uninhibited mild steel surfaces.

## III. EXPERIMENTAL RESULTS

**3.1 Introduction:** The adsorption process is influenced by the phosphonic acid groups present in the inhibitor molecule which forms the protective complex Fe-DMBP and the distribution of charge [12] in the inhibitor molecule on to the metal surface. At higher concentration of DMBP aggressive  $Cl^-$  ion enhances the corrosivity of the metal surface due to desorption of the inhibitor molecules on the surface.

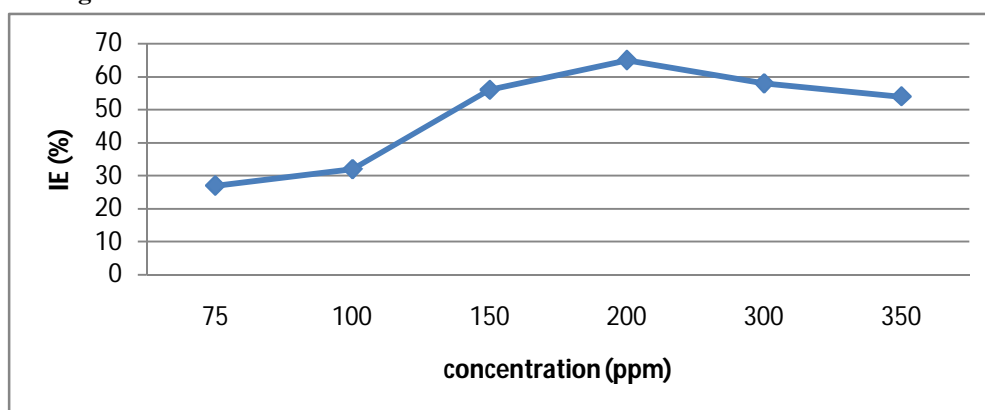
Phosphonic acids can be adsorbed on the mild steel surface by the interaction between lone pair of electron of oxygen and phosphorus atoms of the inhibitor and the metal surface. This process is facilitated by the presence of vacant orbitals of low energy in ion atoms, as observed in the transition metals.

**Table 1:** Corrosion rates of mild steel in neutral aqueous environment ( $Cl^- = 60$  ppm) in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight-loss method.

Inhibitor system: DMBP+ NaCl (60ppm) system      Immersion Time: 3 Hours      pH = 7

S.No	Conc. of DMBP (ppm)	Conc. of $Zn^{2+}$ (ppm)	Wt.loss (g)	CR (mmpy)	Surface coverage ( $\theta$ )	IE (%)
1. Blank	0	0	0.0025	0.9297	-	-
2.	75	0	0.001825	0.6787	0.2700	27
3.	100	0	0.0017	0.6322	0.3200	32
4.	150	0	0.0011	0.4090	0.5600	56
5.	200	0	0.000875	0.3254	0.6500	65
6.	300	0	0.00105	0.3904	0.5800	58
7.	350	0	0.00115	0.4276	0.5400	54

**Figure 1:** Plot of IE of carbon steel as a function of various concentration of DMBP at pH 7



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On analyzing the Table 1. when the concentration of inhibitor DMBP inhibition efficiency increases as shown pictorially in Fig.1 whereas Corrosion rate decreases due the strong adsorption of inhibitor molecules on mild steel surface. The optimum concentration which shows the maximum efficiency of 65% is selected as the best concentration combination for further studies.

### 3.2 Influence of $Zn^{2+}$ ion on IE of DMBP

**Table.2.**Synergistic effect of Zinc ions in the inhibitor formulation

Conc. of DMBP (ppm)	Conc. of $Zn^{2+}$ (ppm)	CR (mmpy)	Surface coverage ( $\theta$ )	IE (%)
0	0	0.9297	-	-
75	90	0.2949	0.6830	68.3
100	90	0.2930	0.6850	68.5
150	90	0.2901	0.6880	68.8
200	90	0.2696	0.7100	71
300	90	0.3068	0.6700	67
350	90	0.2975	0.6800	68

It is observed from the Table 2 that a synergistic effect is exist between DMBP and  $Zn^{2+}$ . For example 90 ppm of  $Zn^{2+}$  has 66.8%. while 200 ppm of DMBP has 65% IE. Interestingly their combination has 71% IE. This suggests that a synergism exist between  $Zn^{2+}$  and DMBP. The combined effect is more pronounced in IE of the inhibitor than its individual ability .

### 3.3 Effect of temperature

Generally temperature rise on adsorption studies increases the kinetic energy of molecules adsorbed on the metal surface and leads to increase in rate of desorption process than adsorption.

**Table 3:** Effect of various temperatures on mild steel corrosion in aqueous medium containing 60 ppm  $Cl^-$  ion.  
Inhibitor system: DMBP – $Zn^{2+}$  (90ppm) Immersion Time: 3 hours

DMBP (ppm)	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	-	1.078	-	1.227	-	1.4132	-	1.599	-	1.822
75	41.4	0.6322	39.4	0.7438	38.9	0.8628	36.7	1.0116	32.6	1.2272
100	55.2	0.4834	51.5	0.5950	49.2	0.7178	48.8	0.8181	42.8	1.0413
150	65.5	0.3719	63.6	0.4463	60.5	0.5578	58.1	0.6694	49	0.9297
200	75.2	0.2677	72.7	0.3347	71.8	0.3979	69.8	0.4835	61.2	0.7066
300	65.9	0.3681	64.2	0.4388	63.1	0.5206	60.4	0.6322	53.1	0.8554
350	55.2	0.4835	51.5	0.5950	49.5	0.7140	46.5	0.8554	40.8	1.0785

The effect of temperature on the inhibitory action of inhibitor is determined by weight loss method at various concentrations at different temperatures ranging from 303 to 343 K are reported in table 5. It is cleared from the table 3 that as the concentration of the inhibitor increases corrosion rate decreased at all temperatures [13] whereas IE

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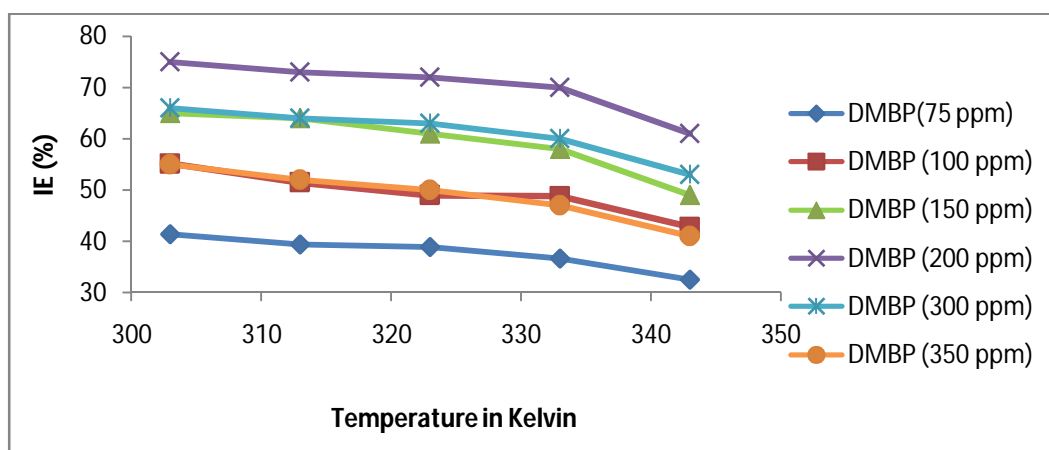
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increases upto 200 ppm concentration of inhibitor, beyond that, at higher temperatures viz. 300 ppm and 350 ppm IE decreases.

**Figure 2 :** A graph is plotted between temperature and inhibition efficiency at temperature ranging from 303 to 343K for different concentration of inhibitor clearly reveals that IE decreases with rise in temperature.

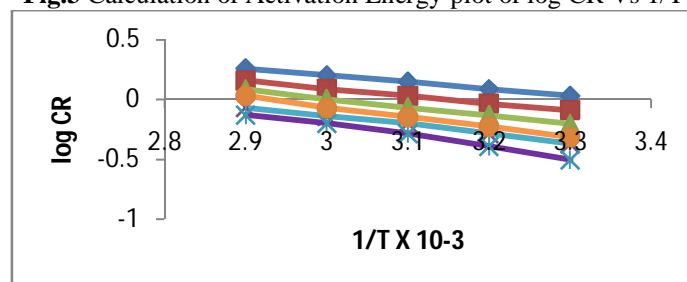
This is due to decrease in adsorption of inhibitor molecule on mild steel surface that would suggest physical adsorption of DMBP on MS.



This may be due to a competition between adsorption over desorption of the inhibitor and hence IE decreases. The optimum temperature is 303K and the maximum efficiency reached is 75.2% for 200 ppm concentration. Further IE decreases in all higher temperatures is due to the physisorption mechanism and increase in kinetic energy of the molecule for every 10°C rise of temperature.

### 3.4 Interpretation of thermodynamic data

**Fig.3** Calculation of Activation Energy-plot of log CR Vs 1/T



The activation energy at different concentration of the inhibitor is calculated by plotting log CR Vs 1/T (Fig 3). According to earlier reports if  $E_a$  values are less than 18 kJ/mol [14,15] which indicates physisorption. In our study  $E_a$  value the increases of concentration of DMBP hinders metal dissolution [16].

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**Table 4:** Activation parameters of the dissolution of mild steel in aqueous medium in the absence and presence of inhibitor system (DMBP-Zn<sup>2+</sup>) at 303K

Inhibitor Conc.(ppm)	E <sub>a</sub> (kJ / mol)	ΔH <sub>a</sub> =E <sub>a</sub> - RT (kJ / mol)	ΔS <sub>a</sub> kJ/mol
0	10.91	-27.48	-240.256
20	11.8	-29.80	-242.17
75	13.57	-34.18	-243.41
150	14.28	-35.97	-246.13
200	17.85	-44.96	-246.74
350	16.33	-41.14	-244.22

The maximum E<sub>a</sub> value in the present study is 17.85 kJ/mol shows inhibitor adsorption follows physisorption.

Thermodynamic data of change in free energy (ΔG<sub>0</sub>) is calculated by using the following formula [ΔG° = -RTln(55.5Kads)] and tabulated in table 5.

**Table 5:** The thermodynamic parameters of adsorption of DMBP-Zn<sup>2+</sup> system on mild steel at various temperatures

Conc. (ppm)	-ΔG <sub>ads</sub> <sup>0</sup> (kJ/mol)				
	303 K	313K	323K	333K	343K
20	17.0849	17.0991	17.0302	16.9728	16.5451
75	15.7704	15.5610	15.5081	15.2724	14.8159
150	21.8342	15.6612	15.4316	15.3747	15.2121
200	16.3818	15.910	15.5265	15.2383	15.1022
350	13.290	12.915	12.7138	12.4111	17.6283

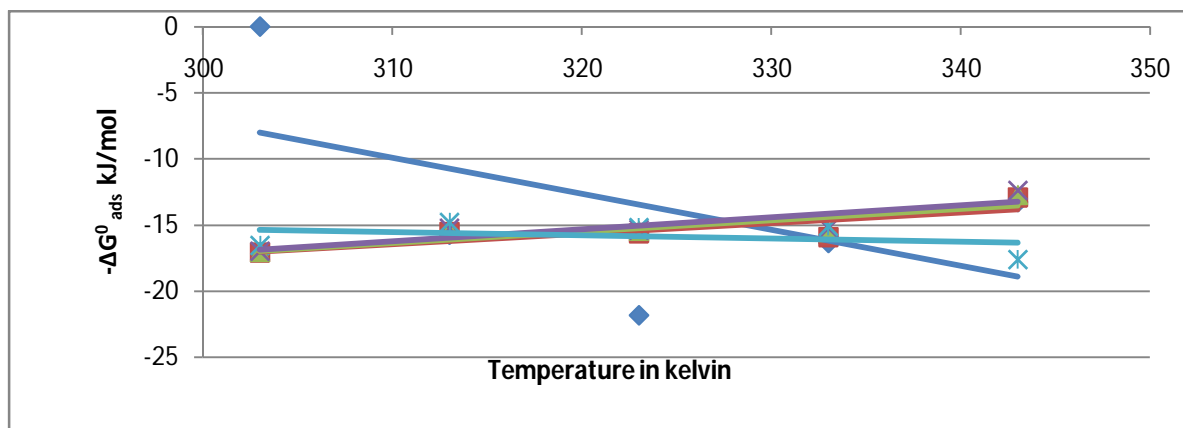
The negative values of ΔG<sub>ads</sub><sup>0</sup> (12.4111- 21.8342 kJ/mol) suggests that the strong interaction of the inhibitor molecule whereas low value of ΔG<sub>ads</sub><sup>0</sup> indicates spontaneous adsorption of inhibitor on MS surface. The enthalpy of adsorption ΔH<sub>ads</sub> is calculated by using the following relation [17] ΔH = Ea - RT and given in table 4. The negative values of ΔH reflect that the process of adsorption on the metal surface is exothermic process. The ΔS<sub>ads</sub> values are calculated by using equation (Intercept from Arrhenius plots) = log R/Nh + ΔS / 2.303 x R] and given in table 4. The negative values of ΔS indicates spontaneous adsorption reaction this indicates that in the rate determining step activated complex represents association rather than dissociation, indicating that ongoing reactant to the activated complex there is decreasing disorder.

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**Fig.4.**Plot of T Vs  $\Delta G^0_{ads}$



The gradual decrease in the -ive value of Gibbs' free energy as shown in the graph.6 indicates more spontaneity with increase in concentration of the inhibitor and facilitate the inhibition process and this condition is unfavorable to corrosion process.

### 3.5 Adsorption isotherm studies

The primary step in the action of inhibitors is the adsorption on the metal surface. Adsorption isotherm values are important to explain the mechanism of corrosion inhibition of organo electrochemical reactions. The most frequently used isotherm are Frundlich, Langmuir, Temkin, Frumkin etc.,. The experimental data in this study are found to fit with Langmuir adsorption isotherm [18] which is expressed by  $\frac{C}{\theta} = \frac{1}{K_{ads}} + C$ , where  $K_{ads}$  is the equilibrium constants of the adsorption –desorption process,  $\theta$  is the surface coverage and C is the concentration of the inhibitor.

**Fig 5** Langmuir adsorption plots for DMBP on MS in aqueous medium

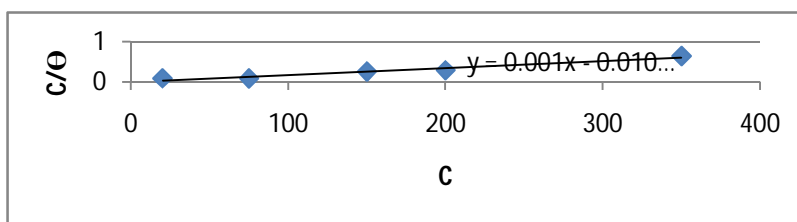


Fig-5 shows the linear plots for C/θ Vs C suggesting that the adsorption obeys the Langmuir adsorption isotherm. The results show that the linear regression coefficient ( $R^2$ ) is almost equal to unity which indicates the existence of molecular adsorption within the adsorbed layer. Moreover the essential characteristic Langmuir isotherm can be expressed in terms of a dimensionless separation factor,  $R_L$  [19] which describes the type of isotherm and is defined by  $R_L = \frac{1}{1+K_{ads}C}$  the smaller  $R_L$  value indicates a highly favorable adsorption. If  $R_L > 1$ , unfavorable;  $R_L = 1$ , Linear;  $0 < R_L < 1$ , favorable; and if  $R_L = 0$ , irreversible.

### 3.6 Electrochemical measurements :Potentiodynamic polarization study

The various electrochemical parameters calculated from Tafel plots (fig 6(a) and 6(b)) are given in table 6. When carbon steel is immersed in aqueous solution containing 60 ppm  $Cl^-$  ion the corrosion potential is -900 mV Vs. SCE. When inhibitors DMBP and  $Zn^{2+}$  are added the corrosion potential is shifted to anodic side (-724 mV Vs. SCE).

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This suggests that this formulation controls anodic reaction predominantly. This is due to more DMBP is transported to the anodic side in the presence of  $Zn^{2+}$ .

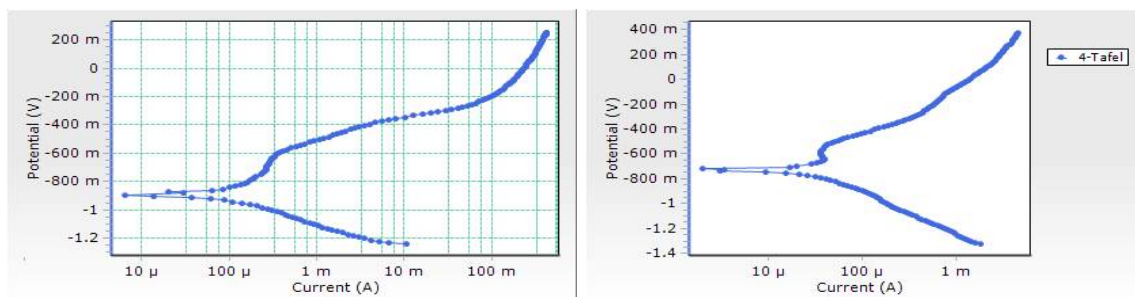
**Table 6:** Electrochemical parameters and IE of mild steel in aqueous medium containing 60 ppm  $Cl^-$  ion and the optimum concentration of DMBP Immersion period:3 hours pH = 7

Conc.of inhibitor system	E <sub>corr</sub> (mV/ SCE)	Tafel polarization parameters			IE (%)
		I <sub>corr</sub> ( $\mu A/cm^2$ )	$\beta_a$ (mV/dec)	$\beta_c$ (mV/dec)	
Blank	-900.203	89.319	260.33	172.2	-
$Cl^-$ ion + $Zn^{2+}$ (90 ppm) + DMBP (200 ppm)	-59.148	18.848	398.645	254.264	78.8

The corrosion current for aqueous solution containing 60 ppm of  $Cl^-$  is  $89 \mu A/cm^2$  as given in the table 6. The corrosion current for formulation consisting of 60 ppm  $Cl^-$ , DMBP (200 ppm),  $Zn^{2+}$  (90 ppm) have decreased to  $28 \mu A/cm^2$ . This is due to the formation of a protective film on the metal surface.

**Fig.6(a)** Tafel plots for sodium chloride

**Fig.6 (b)** Tafel plots for DMBP



Tafel constants ( $\beta_a$ ,  $\beta_c$ ) obtained from cathodic and anodic curves listed in the table 6 suggest that the inhibitors are mixed type and inhibit corrosion by blocking the active sites [20]. The inhibition efficiency obtained from weight loss measurement 71 % is in excellent agreement with the electrochemical study (68%).

### AC impedance study

AC impedance spectra of carbon steel immersed in test solutions containing  $Cl^-$  and inhibitor formulation is recorded in the figure 7. The AC impedance parameters namely charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) are given in Table 7.

**Table7:** AC impedance parameters of mild steel immersed in blank( $Cl^-$ ) and in inhibitor formulation consisting of DMBP+  $Zn^{2+}$  (90 ppm)+  $Cl^-$  ion in aqueous medium.

Inhibitor system	$R_{ct}$ (Ohm)	$C_{dl}$ ( $\mu F/cm^2$ ) $\times 10^{-6}$
$Cl^-$ ion	85.093	18.709
$Cl^-$ ion + $Zn^{2+}$ (90 ppm) + DMBP (200 ppm)	1834.57	3.4554

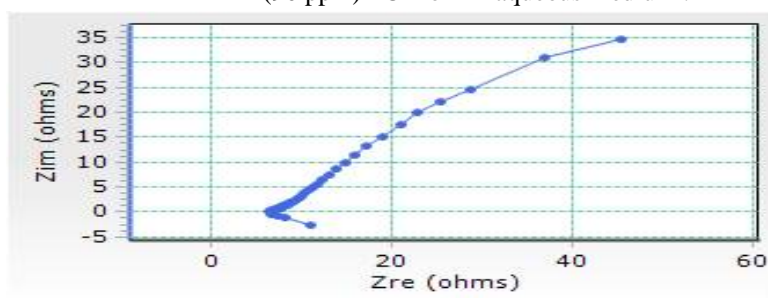
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The aqueous solution containing 60 ppm of  $Cl^-$  ion has  $R_{ct}$  value of  $85.093 \Omega$  and  $C_{dl}$  value of  $18.709 \times 10^{-6} \mu F/cm^2$ . In the presence of DMBP,  $Zn^{2+}$   $R_{ct}$  value increases from  $85.093$  to  $1834.57 \Omega$  and the  $C_{dl}$  value decreases from  $18.709$  to  $3.4554 \times 10^{-6}$ . The shape of the plot suggests that it is a diffusion controlled process. The higher increase in  $R_{ct}$  values indicates the formation of protective film on the metal surface and higher inhibition efficiency.

**Fig. 7.** AC impedance spectra of mild steel immersed in blank( $Cl^-$ ) and in inhibitor formulation consisting of DMBP+  $Zn^{2+}$  (90 ppm)+  $Cl^-$  ion in aqueous medium.

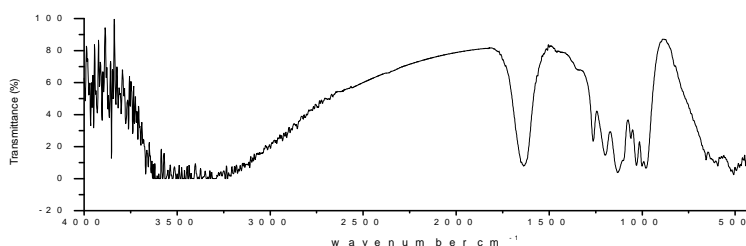


Diffused shape of the AC impedance spectra instead of a perfect semicircle indicates the diffusion controlled inhibition process dominates the charge transfer process.

### 3.7 FTIR Analysis

The FTIR spectrum of pure DMBP is shown in Fig 8. The P-O stretching frequency appears at  $1058 \text{ cm}^{-1}$ . The P-OH group causes absorption at  $1036 \text{ cm}^{-1}$  and P(O)(OH) group at  $3460 \text{ cm}^{-1}$ . The absorption band at  $1058 \text{ cm}^{-1}$  represents P-O stretching frequency. The absorption at  $1299 \text{ cm}^{-1}$  represents P=O stretching. The absorption band due to the bending of O-P-O appears at  $496 \text{ cm}^{-1}$ ,  $569 \text{ cm}^{-1}$  and  $642 \text{ cm}^{-1}$ . The increase in P=O stretching frequency of the ester from  $1299 \text{ cm}^{-1}$  to  $1314 \text{ cm}^{-1}$  relative to the oxides, results from the electro negativity of the attached alkoxy groups. Thus FTIR spectrum of DMBP with molecular formula  $C_{12}H_{19}O_3P$  is characterized by the FTIR spectrum.

**Fig.8** FTIR Spectra of the inhibitor formulation (DMBP- $Zn^{2+}$  and  $Cl^-$ )



The FTIR spectrum of the film formed on the surface of the carbon steel after immersion in the test solution containing DMBP- $Zn^{2+}$  and  $Cl^-$  is shown in Figure 10. The shift P-O frequency from  $1058 \text{ cm}^{-1}$  to  $1044 \text{ cm}^{-1}$  indicates that the oxygen atom of the P-O group has coordinated with  $Fe^{2+}$  resulting in the formation of  $Fe^{2+}$ -DMBP complex formed on the anodic sites of the metal surface. The P=O stretching frequency increased from  $1299 \text{ cm}^{-1}$  to  $1335 \text{ cm}^{-1}$  it also confirms the complex formation between the inhibitor and  $Fe^{2+}$ . The peak at  $3343 \text{ cm}^{-1}$  due to OH stretching. The band due to Zn-O stretch appears at  $1314 \text{ cm}^{-1}$ . These results are confirmed the presence of  $Zn(OH)_2$  deposited on the cathodic sites of the metal surface [21].



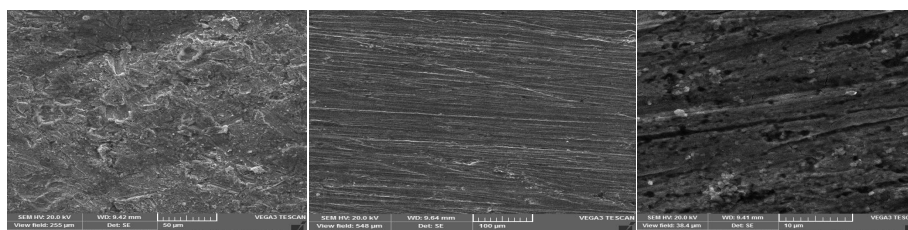
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### 3.8 Surface morphology study

The surface morphologies of carbon steel specimen in aqueous solution containing 60 ppm Cl<sup>-</sup> ion in the presence and absence of inhibitor after 3 hours of immersion period are examined using a Scanning Electronic Microscopy (SEM) is displayed in fig 9-a - 9c



**Fig. 9.**

(a)SEM photograph of polished mild steel      Fig,9 (b)corroded MS      Fig. 9(c) inhibited mild steel

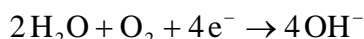
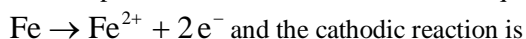
In the absence of inhibitor Fig 11(a) a very smooth surface is obtained due to the absence of corrosive products on the surface. In the presence of 60 ppm Cl<sup>-</sup> ion (corrosive medium) (Fig 11(b)) a very rough surface is observed due to rapid corrosion attack of carbon steel by chloride anions. There are few pits surrounded by iron oxide layer which almost fully covers the carbon steel surface, revealing that pit formation under these conditions occurs continuously during the exposure period while iron oxide builds up over the surface in the presence of the mild steel exposed aqueous medium containing 60 ppm Cl<sup>-</sup> ion and inhibitor solutions (200 ppm DMBP + 90 ppm Zn<sup>2+</sup> ion).

### IV. MECHANISM OF CORROSION INHIBITION

Results of the weight-loss method reveal that the formulation consisting of 60 ppm of Cl<sup>-</sup>, 90 ppm of Zn<sup>2+</sup> and 200 ppm of DMBP offers an inhibition efficiency of 71%. Polarization study shows that this formulation functions like a mixed inhibitor. AC impedance spectra indicate the presence of a protective film on the metal surface. FTIR spectra reveal that the protective film consists of Fe<sup>2+</sup>-DMBP complex and Zn(OH)<sub>2</sub>. SEM images indicate the possibility of formation of protective layer on the metal surface. Thermo dynamical data analysis confirms the physisorption adsorption mechanism and spontaneous, exothermic nature of the inhibition process. Adsorption isothermal studies show that the adsorption process obeys Langmuir adsorption.

In order to explain all these observations in a holistic way, the following mechanism of corrosion inhibition is proposed [22,23,24]

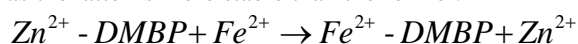
- 1). When mild steel specimen is immersed in the neutral aqueous environment, the anodic reaction is



When the formulation consisting of 60 ppm of Cl<sup>-</sup>, 200 ppm of DMBP,

90 ppm of Zn<sup>2+</sup> is used, the Zn<sup>2+</sup>-DMBP complex formed in solution at pH 7.

- 2). When carbon steel is immersed in this solution the Zn<sup>2+</sup>-DMBP complex diffuses from the bulk of the solution to the metal surface.
- 3). On the metal surface the Zn<sup>2+</sup>-DMBP complex is converted into Fe<sup>2+</sup>-DMBP complex on the local anodic sites as the latter is more stable than the former.<sup>136</sup>



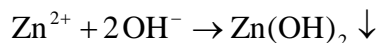
(This reaction takes place in the anodic regions of the metal surface)

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- 4). The released  $Zn^{2+}$  ions combine with  $OH^-$  ions forming  $Zn(OH)_2$  precipitate on the local cathodic sites.



- 5). Thus the protective film consists of  $Fe^{2+}$ -DMBP complex,  $Zn(OH)_2$  and oxides of iron.

## V. CONCLUSION

The following conclusion are drawn from the study:

- Results obtained from the experimental data shows that Diethyl-4-Methyl-Benzyl Phosphonate (DMBP) acts as an effective inhibitor on mild steel in aqueous medium.
- IE increases with increase in inhibitor concentration whereas at constant concentration (200 ppm) maximum IE(71%) is noticed. However IE decreases with rise in temperature and time of immersion. Maximum inhibition efficiency is shown at 3 hours of immersion period for the optimum concentration of 200 ppm DMBP and 90 ppm  $Zn^{2+}$
- Potentiodynamic polarization study and AC impedance spectral study confirm the formation of inhibitive film on metal surface. FTIR spectra c conforms the formation of inhibitor complex  $Fe^{2+}$ -DMBP- $Zn^{2+}$  and  $Zn(OH)_2$ .
- Thermodynamic parameters such as  $\Delta G_{ads}$ ,  $\Delta H_{ads}$ ,  $\Delta S_{ads}$  indicates spontaneous exothermic and physisorption mechanism. Adsorption isothermal study proves that experimental data obeys Langmuir adsorption isotherm. SEM images evidence the formation of the protective film on the metal surface.

## REFERENCES

- [1] Bingru Zhang, Chengjun He, Cheng Wang, Peidi Sun, Fengting Li, Yu Lin (Synergistic corrosion inhibition of environment-friendly inhibitors on the corrosion of carbon steel in soft water). Corrosion Science, 2015; 94: 6-20.
- [2] S.A.Umoren, Y.Li, F.H.Wang (Influence of iron microstructure on the performance of polyacrylic acid as corrosion inhibitor in sulfuric acid solution). Corros.Sci., 2011; 53:1778-1785.
- [3] A.K.Singh., M.A.Quraishi(The effect of some bis-thiadiazole derivatives on the corrosion of mild steel in hydrochloric acid) Corros. Sci., 2010; 77: 37-45.
- [4] H.Amar, J.Benzakour, A.Derja, D.Villeminand B.Moreau (A corrosion inhibition study of iron by phosphonic acids in sodium chloride solution). Journal of Electroanalytical Chemistry, 558: 131-139, 2003.
- [5] Awad H.S. and Turgoose S. (Influence of hardness salts on effectiveness on Zinc-1-Hydroxyethylidene-1,1-Diphosphonic Acid (HEDP) mixtures in inhibiting the corrosion of mild steel in neutral oxygen-containing solutions). Corrosion, 60 (12): 1168-1179, 2004.
- [6] H.S.Awad(The effect of zinc to – HEDP molar ratio on the effectiveness of Zinc-1-Hydroxyethylidene-1,1-Diphosphonic Acid in inhibiting corrosion of carbon steel in neutral solutions). Anti-Corrosion Methods and Materials, 52 (1): 22-28, 2005;
- [7] Y.Gonzalez, M.C.Lafont, N.Pebere and F.Moran ( A synergistic effect between zinc salt and phosphonic acid for corrosion inhibition of a carbon steel). Journal of Applied Electrochemistry, 26 (12): 1259-1265, 1996.
- [8] E.Kálmán, F.H.Kármán, J.Telegdi, B.Várhegyi, J.Balla and T.Kiss (Inhibition efficiency of n-containing carboxylic and carboxy-phosphonic acids). Corrosion Science, 35: 1477-1481, 1993.
- [9] G.Wrangling, Introduction to corrosion and protection of metals, London, UK: Chapman and Hall; 236, 1985.
- [10] A.Singh, B.K.Singh, M.A.Quraishi, RASAYAN Journal of Chemistry, 3,811, 2010.
- [11] A.Y.El-Etre, M.Abdallah, Z.E.El-Tantaway, Corrosion Science, 47, 385, 2005.
- [12] Q.B.Zhang, Y.X.Hua, Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid, ElectrochimicaActa 54, 1881-1887, 2009.
- [13] R.Saratha, S.V.Priya and P.Thilagavathy, Investigation of Citrus aurantiifolia leaves extract as Corrosion Inhibitor for mild steel in 1M HCl, E-Journal of Chemistry, 6 (3), 785-795,2009.
- [14] G.Gunasekaran and L.R.Chaughan, Corrosion inhibition of mild steel by palnt extract in dilute HCl medium, Corrosion Science, 49, 1143-1161, 2007.
- [15] A.A.Siaka, N.O.Eddy, S.O.Idris, A.Muhammed, E.M.Elinge and F.A.Atikel, FTIR Spectroscopic information on the corrosion inhibition potentials of Ampicillin in HCl solution, Innov.Sci.Eng., 2, 41-48, 2012.
- [16] A.M.Ridwan, A.A.Rahim, A.M.Shah, Synergistic Effect of Halide ions on the Corrosion Inhibition of Mild steel in Hydrochloric acid using Mangrove Tannin, Int.J.Electrochem.Sci., 7, 8091-8104, 2012.
- [17] A.S.Fouda, E.L.Haddad and Y.M.Abdallah, Septazole: Antibacterial Drug as a Green Corrosion Inhibitor for Copper in Hydrochloric acid solution, Inter.J.Inno.Res.Sci., 2(12), 7073-7085, 2013.
- [18] Q.Zhang, Y.Hua and Z.Zhou, Corrosion properties of Copper, Nickel and Titanium in AlkylimidazoliumChloroaluminate Based Ionic liquids, Int.J.Electrochem.Sci., 10239-10249, 2013.

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- [19] L.D.Mall, V.C.Srivastara, N.K.Agrawal and I.M.Mishra, Adsorptive removal of Malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analysis, *Colloids surface A: Physicochem.Eng.Aspects*, 264,17-28,2005.
- [20] V.HemaPriya, K.Parameswari and S.Chitra, Anti Corrosion properties of Benzothioazole derivatives for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> solution, *Chem.Sci.Rev.Lett.*, 3(12), 824-835, 2014.
- [21] R.Kalaivani, B.narayanaswamy, J.A.Selvi et.al, *Port. Electrochim. Acta*, 27, 177, 2009.
- [22] T.Horvath, E.Kalman, G.Kutsan and A.Rauscher, *Br.Corr.J.*, 29 , 215, 1994.
- [23] G.Gunasekaran, R.Natarajan and N.Palaniswamy, *Corr.Sci.*, 43, 1615, 2001.
- [24] S.Rajendran, B.V.Apparao and N.Palaniswamy, *Anti-Corro.Methds. and Matls.* 47, 83, 2000.