

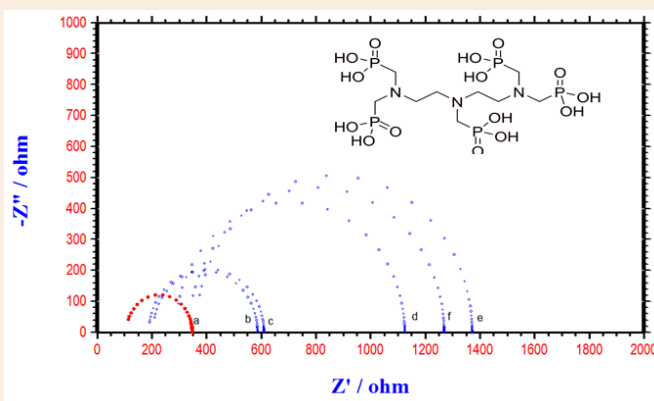
## Research Article

## Electrochemical and Surface Modification Studies of Green Materials

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Tamil Nadu, India.**Abstract**

The corrosion inhibition behaviour of diethylene-triaminepenta(methylene phosphonic acid) (DETPMP) separately and in combination with very low concentration of zinc ions ( $Zn^{2+}$ ) in controlling corrosion of carbon steel immersed in well water was studied using Weight – loss, Potentiodynamic polarization and A.C. impedance techniques. The nature of protective film has been analysed by FTIR spectra. The studies were carried out at room temperature. The surface morphology of the corroded carbon steel samples was studied by scanning electron microscopy. The results show that DETPMP is an effective inhibitor for carbon steel corrosion in well water which is synergistically improved in the presence of  $Zn^{2+}$ . The SEM photographs show a clearly different surface morphology in the presence and absence of inhibitor. The results obtained by potentiodynamic polarization measurements and A.C. impedance studies are consistent with the result of the mass – loss technique. The binary system acts as a cathodic type inhibitor.

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**Keywords:** Carbon steel, corrosion inhibitors, phosphonic acid, mass – loss, FTIR, electrochemical studies, SEM, EDAX.

**Introduction**

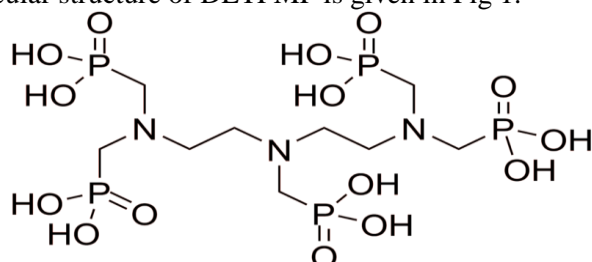
The corrosion of carbon steel is a subject of fundamental, academic and industrial concern and has received a considerable attention during the last few decades [1]. Corrosion, scale and fouling problems can appear when water containing chlorides is used as thermal fluid. This problem can occur jointly, reducing the thermal efficiency of the cooling circuit with the significant social – economic repercussions. To avoid or minimize these problems, water used in cooling circuit is treated with inhibitive formulation. Inhibitors are generally used in these processes to control metal dissolution. Several phosphonic acids have been used as corrosion inhibitors due to their hydrolytic stability, ability to form complex with metal ions and scale inhibiting property [2-6].

The present work was undertaken to investigate the corrosion inhibition behaviour of DETPMP separately and in combination with very low concentration of  $Zn^{2+}$  on carbon steel in well water. The techniques used are weight - loss measurements, potentiodynamic polarization measurements and AC impedance, FTIR and SEM. It was reported, in previous study, that the inhibitive effect of DETPMP –  $Ni^{2+}$  on the corrosion of carbon steel in sea water [7] and synergistic effect of DETPMP in well water by sodium tungstate –  $Zn^{2+}$  system[8].

**Experimental****Materials**

The composition of carbon steel used for corrosion inhibition studies was (Wt %): 0.026% S, 0.06% P, 0.4% Mn, 0.1% C and balance being Fe. The specimens of size 1.0cm×4.0cm×0.2cm were press cut from the carbon steel sheet, were machined and abraded with a series of emery papers. This was followed by rinsing in acetone and bidistilled water and finally dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage. The inhibitors DETPMP, molecular mass  $573.20\text{g mol}^{-1}$ ,  $Zn^{2+}$  ions were used as received. A stock solution of 1000ppm of DETPMP was prepared in bidistilled water and the desired concentration was obtained by appropriate dilution. The concentration of DETPMP used for the study ranges from

10 to 150ppm. All solutions were using well water (Tiruchirappalli, Tamil Nadu, India). The study was carried out at room temperature. The molecular structure of DETPMP is given in Fig 1.



**Figure 1.** Molecular structure of DETPMP

### Weight - loss Measurements

The freshly prepared carbon steel specimens were suspended in 150ml beakers containing 100ml of test solution maintained at room temperature with the aid of glass rods and hooks. The weight loss taken was the difference between the weight at a given time and the original weight of the specimens. The measurements were carried out for the uninhibited solution and the solution containing DETPMP and DETPMP – Zn<sup>2+</sup> mixture. Weight loss experiments were performed for the duration of seven days. The specimens were immersed in triplicate and the average corrosion rate was calculated. These uncertainties or RSD for three replicate measurements were less than 5%. The corrosion rates ( $C_R$ ) were determined using the equation:

$$CR \left( \frac{mm}{y} \right) = \frac{87.6 \times w}{a t D} \quad (1)$$

where  $w$  = corrosion weight loss of carbon steel (mg)

$a$  = area of the coupon (cm<sup>2</sup>)

$t$  = exposure time (h)

$D$  = density of the carbon steel (g cm<sup>-3</sup>).

The inhibition efficiency (IE) of DETPMP, Zn<sup>2+</sup> mixture was calculated by using the following equation:

$$\%IE = \frac{C_{R_0} - C_{R_i}}{C_{R_0}} \times 100 \quad (2)$$

where  $C_{R_0}$  = corrosion rate of carbon steel in the absence of inhibitor

$C_{R_i}$  = corrosion rate of carbon steel in the presence of inhibitor

### Surface analysis by FTIR spectroscopy

After the immersion period of one day in various environments, the specimens were taken out of the test solution and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout. FTIR spectrum of the powder (KBr Pellets) was record using perkin-elmer-1600 FTIR spectrophotometer with resolving power of 4 cm<sup>-1</sup>.

### Electrochemical studies

Both the potentiodynamic polarization studies and electrochemical impedance spectroscopic (EIS) studies were carried out using the electrochemical workstation model CHI- 760d and the experimental data were analysed by using the electrochemical software (Version: 12.22.0.0). The measurements were conducted in a conventional three electrode cylindrical glass cell with platinum electrode as auxiliary electrode and saturated calomel electrode as reference electrode. The working electrode was carbon steel embedded in epoxy resin of polytetrafluoroethylene so that the flat surface of 1cm<sup>2</sup> was the only surface exposed to the electrolyte. The three electrodes set up was immersed in control solution of volume 100ml both in the absence and presence of the inhibitors formulations and allowed to attain a stable open circuit potential (OCP). The pH values of the solution were adjusted to 7.0 and the solutions were unstirred during the experiments.

Polarization curves were recorded in the potential range of -750 to -150 mV with a resolution of 2mV. The curves were recorded in the dynamic scan mode with a scan rate of  $2\text{mVS}^{-1}$  in the current range of -20mA to +20mA. The Ohmic drop compensation has been made during the studies. The corrosion potential ( $E_{\text{corr}}$ ), corrosion current ( $I_{\text{corr}}$ ), anodic Tafel slope ( $\beta_a$ ) and cathodic Tafel slope ( $\beta_c$ ) were obtained by extrapolation of anodic and cathodic regions of the Tafel plots. The inhibition efficiency ( $IE_p$ ) values were calculated from the  $I_{\text{corr}}$  values using the equation [9].

$$IE_p(\%) = [1 - (I'_{\text{corr}}/I_{\text{corr}})] \times 100 \quad (3)$$

Where  $I_{\text{corr}}$  and  $I'_{\text{corr}}$  are the corrosion current densities in case of control and inhibited solutions respectively. Electrochemical impedance spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 60KHz to 10MHz with 4 to 10 steps per decade. A sine wave, with 10mV amplitude, was used to perturb the system. The impedance parameters viz., charge transfer resistance ( $R_{\text{ct}}$ ), double layer capacitance ( $C_{\text{dl}}$ ) were obtained from the Nyquist plots. The inhibition efficiencies ( $IE_i$ ) were calculated using the equation,

$$IE_i(\%) = 100 [1 - R_{\text{ct}}/R'_{\text{ct}}] \quad (4)$$

where  $R_{\text{ct}}$  and  $R'_{\text{ct}}$  are the charge transfer resistance values in the absence and presence of the inhibitor respectively.

### Scanning Electron Microscopy

The surface morphology of the corroded steel sample surface in the presence and absence of the inhibitors was studied using SEM (Model: TESCAN vega3 USA). To study the surface morphology of carbon steel, polished specimens prior to initiation of any corrosion reaction, were examined in optical microscope to find out any surface defect, such as prior noticeable irregularities like cracks etc. Only those specimens, which had a smooth pit-free surface, were subjected to immersion. The specimens were immersed for 24h at  $30^{\circ}\text{C}$ . After completion of the tests specimens were thoroughly washed with bidistilled water and dried and then subjected to SEM examination.

### Energy Dispersive Analysis of X-ray (EDAX)

EDAX (Model: BRUKER Nano Germany) system attached with Scanning Electron Microscope was used for elemental analysis or chemical characterization of the film formed on the carbon steel surface. As a type of spectroscopy, it relies on the investigation of sample through interaction between electromagnetic radiation and the matter. So that, a detector was used to convert X-ray energy into voltage signals. This information is sent to a pulse processor, which measures the signals and passed them into an analyzer for data display on the analysis.

## Results and Discussion

### Weight - loss Measurements

The corrosion behaviour of carbon steel in well water in the absence and presence of different concentration of DETPMP alone and in combination with  $\text{Zn}^{2+}$ , was studied using a weight – loss technique and data obtained after seven days of immersion are shown in Table 1. The IE increases with increasing DETPMP concentrations showing a maximum IE of 30% at 125ppm. The increased IE with increasing inhibitor concentrations indicated that more DETPMP molecules are adsorbed on the carbon steel surface at higher concentrations leading to greater surface coverage and hence the formation of a protective film [10]. A relatively low IE at lower concentrations of DETPMP could be attributed to the modest surface coverage owing to its small molecular area and solubility of adsorbed intermediate formed on the surface. A further increase in DETPMP concentrations causes a slight lowering in IE. This phenomenon is attributed to the dissolution of adsorbed inhibitor film [11].

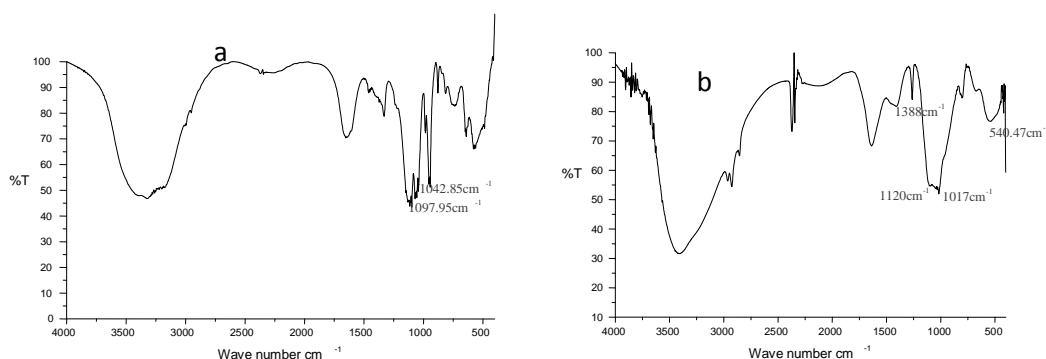
To observe the effect of  $\text{Zn}^{2+}$  on the corrosion inhibition behaviour of DETPMP, the corrosion of carbon steel in well water in the absence and presence of different concentrations of DETPMP, in combination with 10ppm  $\text{Zn}^{2+}$  was separately studied. The results are shown in Table 1. The corrosion rates of carbon steel in the presence of DETPMP in combination with  $\text{Zn}^{2+}$  are further reduced. In comparison, DETPMP alone 30% IE and 10ppm  $\text{Zn}^{2+}$  alone 11% IE and combinations of binary formulation was 86% IE in this increasing IE effect was synergism ( $S_i$ ) [12-13].

Table 1. Corrosion Rates (CR) of carbon steel in well water, in the Absence and the Presence of Inhibitors and Inhibition Efficiencies (IE) obtained by Weight - Loss Method

Conc. of Zn <sup>2+</sup> (ppm)	Conc. of DETPMP (ppm)	C <sub>R</sub> (mmy <sup>-1</sup> )	IE (%)	Surface coverage	S <sub>1</sub>
Blank	-	194.4	-	-	-
10	-	173.0	11	0.11	-
-	125	136.1	30	0.30	-
10	10	128.3	34	0.34	1.32
10	25	120.5	38	0.38	1.34
10	50	109.0	44	0.44	1.44
10	75	81.6	58	0.58	1.86
10	100	54.4	72	0.72	2.38
10	125	27.2	86	0.86	4.45
10	150	38.8	80	0.80	3.29

### FTIR Spectra

The FTIR absorption spectrum of the surface film formed on carbon steel in presence of binary inhibitors formulation, Zn<sup>2+</sup> 10ppm + DETPMP 125ppm, is shown in the Fig. 2b. This spectrum compared with FTIR spectrum of pure DETPMP in KBr pellet Fig. 2a. The reflection absorption FTIR spectrum of the surface film can be interpreted as follows. The peak due to P-O stretching frequency appears at 1017cm<sup>-1</sup> and C-N stretching frequency appear at 1097cm<sup>-1</sup>. The FTIR spectrum of the film formed on the metal surface after immersion in well water containing 10ppm Zn<sup>2+</sup> and 125ppm DETPMP is shown in Fig. 1b. The P-O stretching frequency has shifted from 1017cm<sup>-1</sup> to 1042cm<sup>-1</sup> and the C-N stretching frequency has shifted from 1097cm<sup>-1</sup> to 1120cm<sup>-1</sup>. This shift indicates that the oxygen and nitrogen atoms of phosphonic acid are coordinated to form Fe<sup>2+</sup> - DETPMP complex on the anodic sites of the metal surface. The peak due to Zn - O appears at 1388cm<sup>-1</sup>. The peak observed at 540.47cm<sup>-1</sup> in the spectrum of the surface film can be assigned to amorphous oxide Fe<sub>2</sub>O<sub>3</sub> [14]. These results confirm the presence of Zn (OH)<sub>2</sub> deposited on the cathodic site of the metal surface. Thus, FTIR spectral study leads to the conclusion that the protective film consists of Fe<sup>2+</sup> - DETPMP complex, Zn (OH)<sub>2</sub> and oxides of Fe.

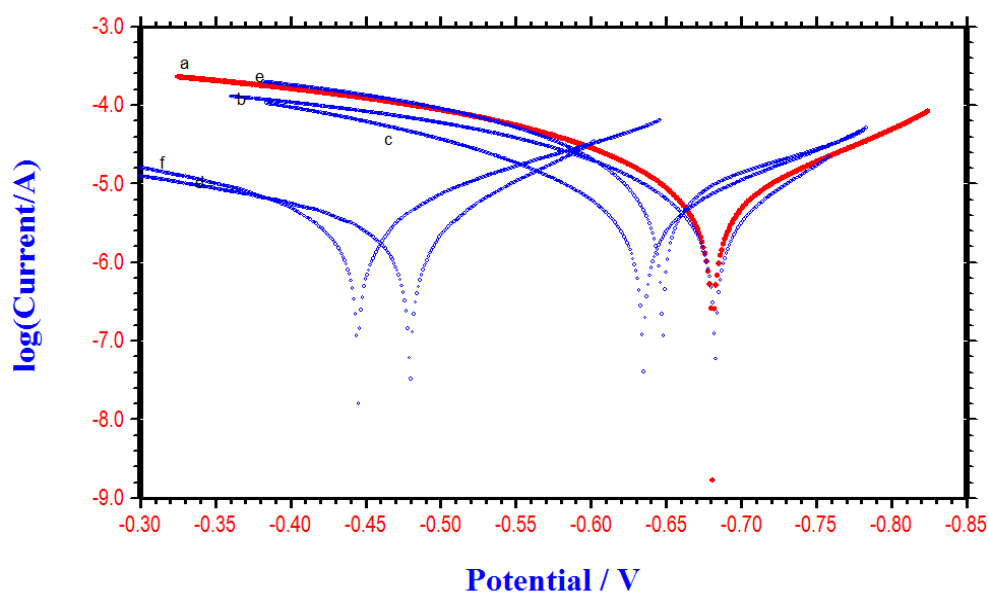


**Figure 2.** a) FTIR Spectrum of pure DETPMP b) Film formed on metal surface after immersion in well water containing 125ppm DETPMP and 10ppm Zn<sup>2+</sup>

### Analysis of Polarization Curves

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. 3. The corrosion parameters are given in Table 2. When carbon steel is immersed in well water the corrosion potential is -0.6884mV Vs SCE (saturated Calomel Electrode). The corrosion current is  $8.705 \times 10^{-4}$  A/cm<sup>2</sup>. When DETPMP 10ppm and Zn<sup>2+</sup>10ppm, DETPMP 50ppm and Zn<sup>2+</sup>10ppm, DETPMP 100ppm and Zn<sup>2+</sup>10ppm, DETPMP 125ppm and Zn<sup>2+</sup>10ppm, DETPMP 150ppm and Zn<sup>2+</sup>10ppm, are added to the above systems the corrosion potentials shift to the cathodic side (-0.6830mV, -0.6390mV, -0.4801mV, -0.6483mV, -0.4456mV). This suggests that this formulation control the cathodic reaction predominately. In the presence of this inhibitors systems, the corrosion current decreases from  $8.705 \times 10^{-4}$  A/cm<sup>2</sup>,  $5.749 \times 10^{-4}$  A/cm<sup>2</sup>,

$4.897 \times 10^{-4} \text{ A/cm}^2$ ,  $2.946 \times 10^{-4} \text{ A/cm}^2$ ,  $1.148 \times 10^{-4} \text{ A/cm}^2$ ,  $1.656 \times 10^{-4} \text{ A/cm}^2$ . The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.



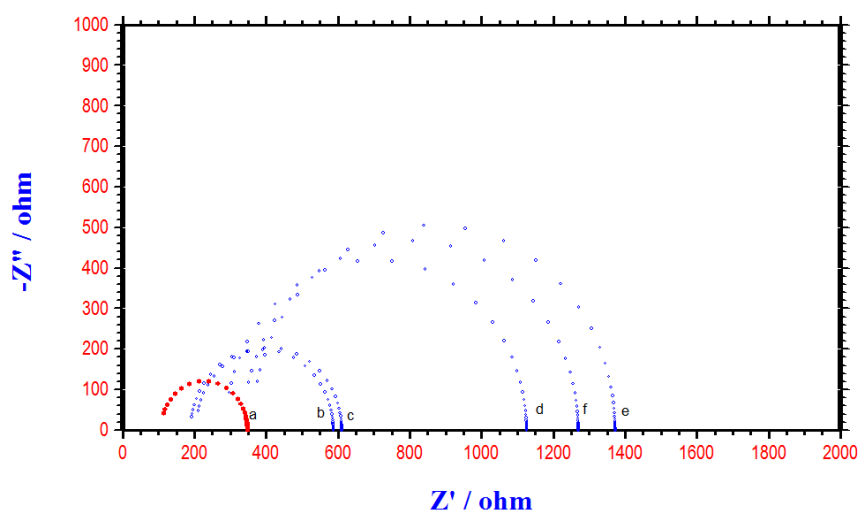
**Figure3.** Potentiodynamic polarization curves for carbon steel in well water in the absence and presence of various inhibitor components (a) Blank (No inhibitor), (b)  $\text{Zn}^{2+}$  (10ppm) + DETPMP (10ppm), (c)  $\text{Zn}^{2+}$  (10ppm) + DETPMP (50ppm) + (d)  $\text{Zn}^{2+}$  (10ppm) + DETPMP (100ppm) + (e)  $\text{Zn}^{2+}$  (10ppm) + DETPMP (125ppm) + (f)  $\text{Zn}^{2+}$  (10ppm) + DETPMP (150ppm).

**Table2.** Tafel parameters for carbon steel in well water in the absence and presence of the inhibitor formulations.

Inhibitor formulation, ppm		Tafel parameters				
$\text{Zn}^{2+}$	DETPMP	$-E_{\text{corr}}$ , mV vs. SCE	$b_a$ , mV dec $^{-1}$	$b_c$ , mV dec $^{-1}$	$I_{\text{corr}}$ , A. $\text{Cm}^{-2}, \times 10^{-4}$	$\text{IE}_p$ , %
-	-	0.6884	6.208	7.208	8.705	-
10	10	0.6830	4.403	14.591	5.749	33.9
10	50	0.6390	6.933	7.513	4.897	43.7
10	100	0.4801	4.226	9.433	2.946	72.0
10	125	0.6485	5.642	5.889	1.148	86.0
10	150	0.4456	6.241	5.890	1.656	80.0

### AC impedance spectra

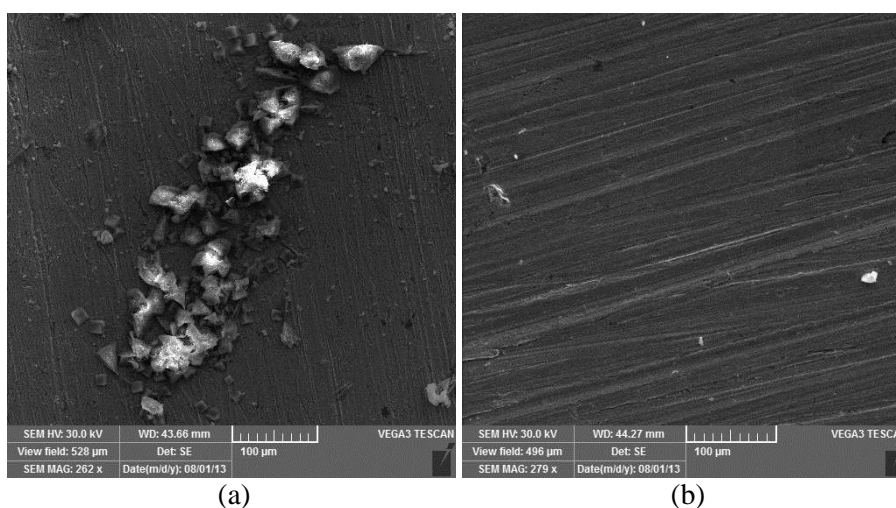
The AC impedance (EIS) spectra of carbon steel under our study are shown in Fig. 4. The AC impedance parameters, namely the charge transfer resistance ( $R_{\text{ct}}$ ) and the double layer capacitance ( $C_{\text{dl}}$ ) are given in Table 3. When carbon steel is immersed in well water, the  $R_{\text{ct}}$  is found to be  $240.0 \Omega \text{ cm}^2$  and the  $C_{\text{dl}}$  value is  $5.4428 \times 10^{-6} \text{ F/cm}^2$ . When 10ppm of  $\text{Zn}^{2+}$  and 10ppm of DETPMP, 10ppm of  $\text{Zn}^{2+}$  and 50ppm of DETPMP, 10ppm of  $\text{Zn}^{2+}$  and 100ppm of DETPMP, 10ppm of  $\text{Zn}^{2+}$  and 125ppm of DETPMP, 10ppm of  $\text{Zn}^{2+}$  and 150ppm of DETPMP are added the  $R_{\text{ct}}$  values has increased tremendously from  $240.0 \Omega \text{ cm}^2$  to  $364.2 \Omega \text{ cm}^2$ ,  $407.4 \Omega \text{ cm}^2$ ,  $839.0 \Omega \text{ cm}^2$ ,  $1540.0 \Omega \text{ cm}^2$ ,  $1231.1 \Omega \text{ cm}^2$  and  $C_{\text{dl}}$  values decreases  $5.4428 \times 10^{-6} \text{ F/cm}^2$  to  $2.4009 \times 10^{-6} \text{ F/cm}^2$ ,  $1.9084 \times 10^{-6} \text{ F/cm}^2$ ,  $0.5081 \times 10^{-6} \text{ F/cm}^2$ ,  $0.1328 \times 10^{-6} \text{ F/cm}^2$ ,  $0.2044 \times 10^{-6} \text{ F/cm}^2$  respectively. The increased  $R_{\text{ct}}$  and decreased  $C_{\text{dl}}$  values obtained from impedance studies justify the good performance of a compound as an inhibitor in well water [15]. This behaviour shows that the film obtained acts as a barrier to the corrosion process that clearly proves the existence and formation of the film.



**Figure4.** Nyquist plots for carbon steel in well water in the absence and presence of various inhibitor components (a) Blank (No inhibitor), (b)  $Zn^{2+}$  (10ppm) + DETPMP (10ppm), (c)  $Zn^{2+}$  (10ppm) + DETPMP (50ppm) +(d)  $Zn^{2+}$  (10ppm) + DETPMP (100ppm) + (e)  $Zn^{2+}$  (10ppm) + DETPMP (125ppm) + (f)  $Zn^{2+}$  (10ppm) + DETPMP (150ppm).

**Table3.** Impedance parameters for carbon steel in well water in the absence and presence of the inhibitor formulations

Inhibitor formulation, ppm		Impedance parameters		$IE_i$ , %
$Zn^{2+}$	DETPMP	$R_{ct}$ , $\Omega.cm^2$	$C_{dl}$ , $F.cm^{-2} \times 10^{-6}$	
Blank	-	240.2	5.4428	-
10	10	364.2	2.4009	34.1
10	50	407.4	1.9084	41.0
10	100	839.0	0.5081	71.3
10	125	1540.0	0.1328	84.4
10	150	1231.1	0.2044	80.5



**Figure 5. a)** SEM image of surface of carbon steel after immersion for 24 h in well water **b)** SEM image of surface of carbon steel after immersion for 24 h in well water in presence of 10ppm  $Zn^{2+}$  and 125ppm DETPMP

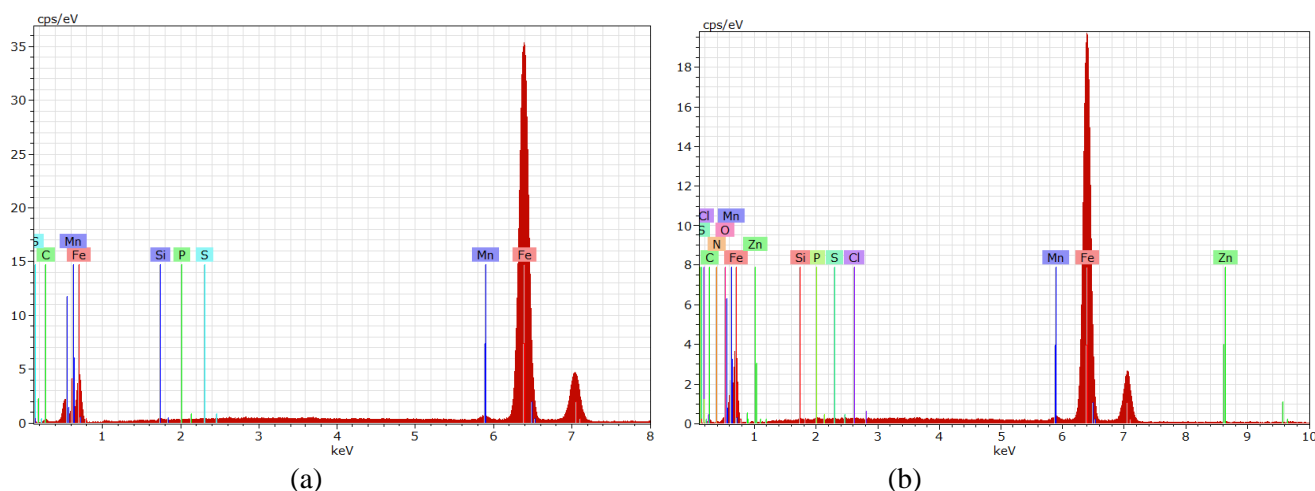
### Scanning Electron Microscopy

SEM was applied to confirm that self- assembled film on the iron surface which can protect the metal from corrosion. The images of carbon steel surface immersed in well water in the absence and presence of (10ppm  $Zn^{2+}$

and 125ppm DETPMP) inhibitors for 24hours are given in Fig. 5. Fig.5a shows an image of carbon steel surface after immersion in well water. The micrograph reveals that the surface is highly damaged in absence of the inhibitors. Fig. 5b shows an image of another carbon steel surface immersed in well water for the same period in presence of (10ppm  $Zn^{2+}$  and 125ppm DETPMP) inhibitor. It could be seen that in presence of the inhibitor, the rate of corrosion was suppressed; it revealed that there was a good protective film adsorbed on specimen's surface, which was responsible for the inhibition of corrosion.

### Energy Dispersive X-ray Analysis (EDAX)

The protective film formed on carbon steel surface was analyzed using EDX as shown in Fig. 6. The EDAX spectrum of polished carbon steel sample shows good surface properties (Fig 6a). The addition of 10 ppm  $Zn^{2+}$  and 125 ppm DETPMP, decreases iron peak and appearance of O, P, N, C and Zn peak was observed due to the formation of a strong protective film of the inhibitor molecules on the surface of carbon steel sample [16] as indicated in Fig. 6b.



**Figure 6.** EDAX image of surface of carbon steel samples: (a) polished carbon steel surface. (b) after immersion for 24 h in well water in presence of 10ppm  $Zn^{2+}$  and 125ppm DETPMP

### Conclusions

The main conclusions of the present study could be summarized as given below:

- 1) Inhibition efficiency (86%) obtained from weight loss data are comparable with those obtained from polarization and AC impedance measurements and it was that they are in good agreement.
- 2) FTIR spectra show that the protective film consists of  $Fe^{2+}$ - DETPMP complex and  $Zn(OH)_2$  and oxides of Fe. AC impedance spectra reveal that a protective film is formed on the metal surface.
- 3) Potentiodynamic polarization studies show that the selected compound suppresses the cathodic process and thus acts as a cathodic inhibitor.
- 4) The results of EIS indicate that the values of  $C_{dl}$  tend to decrease and both  $R_{ct}$  and  $IE_i$ , % tends to increase the inhibitor concentration.
- 5) SEM and EDAX observations of the carbon steel surface show that a film of inhibitor molecules is formed on the carbon steel surface.

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