



# THE INHIBITIVE EFFECT OF DIETHYLENTRIAMINE-PENTAMETHYLENPHOSPHONIC ACID ON THE CORROSION OF CARBON STEEL IN SEA WATER

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The inhibition of the corrosion of carbon steel in sea water by diethylene triamine pentamethylene phosphonic acid (DTPMP) and Ni<sup>2+</sup> has been investigated using weight loss and electrochemical measurements. The results show that 70% inhibition efficiency is achieved with binary system consisting of 250 ppm of DTPMP and 50 ppm of Ni<sup>2+</sup>. Polarization curves indicate that the system functioned as a cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. The protective film has been analysed by FTIR spectra. The surface morphology and the roughness of the metal surface have been analysed by atomic force microscopy.

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## INTRODUCTION

Sea water is a complex natural electrolyte. Sea water contains many corrosive electrolytes such as sodium chloride, magnesium chloride, calcium chloride, etc.; hence, carbon steel immersed in sea water is corroded slowly because of chemical reactions between the metal and the electrolytes.<sup>1-3</sup> Corrosion is the gradual destruction of material, usually metal, by chemical reaction with its environment. The corrosion is severe due to the presence of chloride ions and dissolved oxygen. Sea water has been used as cooling fluid in various industries. Carbon steel is widely used in infrastructure in marine environments.<sup>4</sup> It is one of the major constituents in structural steel applications including body of a ship, offshore platforms, foundation piling, sheet piling, and coastal facilities. It is also used in industry where the metal is exposed to acid corrosion. So, it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used in sea water. Inhibition of corrosion and scaling can be done by the application of inhibitors, which is one of the most practical and economic methods for protection against metallic corrosion.<sup>5,6</sup> Corrosion inhibitors disclose that most organic substances used as corrosion inhibitors can adsorb on the metal surface employed through heteroatoms such as nitrogen, oxygen, sulphur, and phosphorus, multiple bonds or aromatic rings and block the active sites decreasing the corrosion rate.<sup>15</sup> Several phosphonic acids have been used as corrosion inhibitor.<sup>7-9</sup> Our co-workers have conducted various research works using phosphonic acids as an

inhibitor.<sup>10</sup> Phosphonic acids are organic compounds containing R-PO(OH)<sub>2</sub> or R-PO(OR)<sub>2</sub> groups. They are effective chelating agents that are used in cooling water and desalination systems to inhibit scale formation and corrosion. Phosphonic acids are extensively used now-a-days due to their complex forming abilities, high stability under harsh conditions, and low toxicity.<sup>11</sup> They are also used as corrosion inhibitors in concrete, coating, rubber blends, acids cleaners and anti-freeze coolants.<sup>12,13</sup> The inhibition efficiency of phosphonates depends on the number of phosphono groups in a molecule and also on different substituents. Compounds with a phosphonic functional group are considered to be the most effective chemical for inhibiting the corrosion process and it is well known that short-chain-substituted phosphonic acids are good corrosion inhibitors for iron and low-alloyed steels.<sup>14</sup>

The present study aims **a)** to find out the corrosion inhibition effects of diethylene triamine pentamethylene phosphonic acid (DTPMP) and Ni<sup>2+</sup> system on carbon steel in sea water using weight-loss method **b)** electrochemical techniques provide information on the corrosion rate, as well as on processes at interfaces affected by additives **c)** to analyse the protective film by Fourier Transform Infrared Spectroscopy (FTIR) **d)** to study the surface morphological changes during iron corrosion by Atomic Force Microscopy (AFM) **e)** to propose a suitable mechanism of corrosion inhibition based on the results from the above studies.

## EXPERIMENTAL

### Preparation of Specimen

Carbon steel specimen [0.0267 % S, 0.06 % P, 0.4 % Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

### Weight-Loss Method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the absence and presence of  $\text{Ni}^{2+}$  (as  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke's solution.<sup>16</sup> The inhibition efficiency ( $IE$ , in %) was then calculated using the equation:

$$IE = 100 \left( 1 - \frac{W_2}{W_1} \right) \quad (1)$$

where  $W_1$  is the weight loss value in the absence of inhibitor and  $W_2$  is the weight loss value in the presence of inhibitor.

### Polarization Study

Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. The exposed surface area was  $1 \text{ cm}^2$ . A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

### AC impedance spectra

The instrument used for polarization study was also used for AC impedance spectra. The cell set up was the same as that was used for polarization measurements. The real part ( $Z'$ ) and the imaginary part ( $Z''$ ) of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initial  $E_{(v)} = 0 \text{ V}$ , high frequency limit was  $1 \times 10^5 \text{ Hz}$ , low frequency limit was  $1 \text{ Hz}$ , amplitude =  $0.005 \text{ V}$  and quiet time  $t_q = 2 \text{ s}$ . The values of charge transfer resistance,  $R_t$ , and the double layer capacitance,  $C_{dl}$ , were calculated.

$$C_{dl} = \frac{1}{2} I R f_{max} \quad (2)$$

where  $f_{max}$  is maximum frequency.

### Surface Examination Study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analysed by various surface analysis techniques.

### Fourier Transform Infrared Spectra (FTIR)

The FTIR spectra were recorded in a Perkin-Elmer-1600 spectrophotometer. The film formed on the metal surface was carefully removed and mixed thoroughly with KBr making the pellet.

### Atomic Force Microscopy

Atomic Force Microscope (AFM) is an exciting new technique that allows surface to be imaged at higher resolutions and accuracies than ever before. The microscope used for the present study was PicoSPM Molecular Imaging, USA make. Polished specimens prior to the initiation of all corrosion experiments were examined through an optical microscope to find out any surface defects such as pits or noticeable irregularities like cracks, etc. Only those specimens, which had a smooth, pit-free surface were subjected for AFM examination. The protective film formed on the carbon steel specimens after immersion in the inhibitor systems for different time durations were examined for a scanned area of  $30 \times 30 \mu\text{m}^2$  and  $15 \times 15 \mu\text{m}^2$ . The two-dimensional and three-dimensional topography of surface films gave various roughness parameters of the film.

## RESULTS AND DISCUSSION

The physicochemical parameters of sea water used in the present study are given in Table 1.

**Table 1.** The physicochemical parameters of natural sea water collected in Mandapam, Tamilnadu, India.

Parameter	Value
Total dissolved salts ( $\text{mg L}^{-1}$ )	78136
Electrical conductivity ( $\mu\Omega^{-1} \text{ cm}^{-1}$ )	70788
pH	7.82
Total hardness ( $\text{CaCO}_3$ equivalent)	24500
Calcium as $\text{Ca}^{2+}$ ( $\text{mg L}^{-1}$ )	2200
Magnesium as $\text{Mg}^{2+}$ ( $\text{mg L}^{-1}$ )	1800
Sodium as $\text{Na}^+$ ( $\text{mg L}^{-1}$ )	9600
Chloride as $\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	23100
Fluoride as $\text{F}^-$ ( $\text{mg L}^{-1}$ )	1.2
Potassium ( $\text{mg L}^{-1}$ )	900
Sulphate as $\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	2350

### Weight-Loss Method

Table 2 gives values of the corrosion inhibition efficiencies and the corresponding corrosion rates of diethylene triamine pentamethylene phosphonic acid (DTPMP)- $\text{Ni}^{2+}$  system in controlling corrosion of carbon steel in sea water for a period of 24 hours. The DTPMP alone has high rate of corrosion. The inhibition efficiency of DTPMP is improved by adding various concentrations of  $\text{Ni}^{2+}$ . Similar observations have been made by Umamathi et al<sup>17</sup> where they have improved the inhibition efficiency of  $\text{Na}_3\text{PO}_4$  on EDTA by addition of  $\text{Zn}^{2+}$  ion. Mary Anbarasi and Rajendran<sup>18</sup> have improved the inhibition efficiency of heptane sulphonic acid by addition of  $\text{Zn}^{2+}$  ion. However, with increasing the concentration of DTPMP as well as  $\text{Ni}^{2+}$ , the maximum inhibition is achieved and the corrosion rate is decreased. It is found that 250 ppm of DTPMP and 50 ppm of  $\text{Ni}^{2+}$  has 70% inhibition efficiency. The inhibition efficiency increases with the increase of concentration of inhibitors. This behaviour could be attributed to the increase of the surface area covered by the adsorbed molecules of phosphonic acid with the increase of its concentration.

**Table 2.** The inhibition efficiency ( $IE\%$ ) and the corrosion rate ( $\text{mm y}^{-1}$ ) of DTPMP –  $\text{Ni}^{2+}$  system determined by weight-loss method.

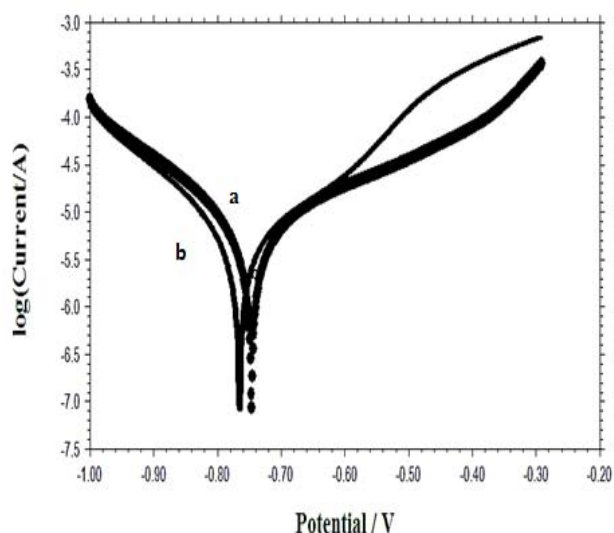
DTPMP, ppm	$\text{Ni}^{2+}$ (ppm)					
	0		25		50	
	$IE, \%$	$CR, \text{mm y}^{-1}$	$IE, \%$	$CR, \text{mm y}^{-1}$	$IE, \%$	$CR, \text{mm y}^{-1}$
0	-	0.1858	8	0.1709	15	0.1579
50	20	0.1486	43	0.1059	52	0.0892
100	28	0.1338	47	0.0985	56	0.0818
150	39	0.1133	52	0.0892	61	0.0725
200	46	0.1003	56	0.0818	66	0.0632
250	50	0.0929	60	0.0743	70	0.0557

**Table 3.** Corrosion parameters of carbon steel immersed in sea water in the presence and absence of inhibitor obtained by polarization method.

Systems	$E_{\text{corr}}, \text{mV vs SCE}$	$I_{\text{corr}}, \text{A cm}^{-2}$	$b_a, \text{mV dec}^{-1}$	$b_c, \text{mV dec}^{-1}$	$LPR, \text{ohm cm}^2$
Sea water	-746	$6.351 \times 10^{-6}$	228	157	$6.356 \times 10^3$
Sea water + DTPMP (250 ppm) + $\text{Ni}^{2+}$ (50 ppm)	-765	$5.238 \times 10^{-6}$	206	148	$7.148 \times 10^3$

### Potentiodynamic Polarization Study

Polarization study has been used to detect the formation of protective film on the metal surface.<sup>19-22</sup> The polarization curves of carbon steel immersed in various test solutions are shown in Fig.1. The cathodic branch represents the oxygen reduction reaction, while the anodic branch represents the iron dissolution reaction. The corrosion parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), Tafel slopes ( $b_c$  and  $b_a$ ) and linear polarization resistance ( $LPR$ ) are given in Table 3.

**Figure 1.** Polarization curves of carbon steel immersed in a) sea water b) sea water + DTPMP 250 ppm +  $\text{Ni}^{2+}$  50 ppm.

When carbon steel is immersed in sea water, the corrosion potential is  $-746 \text{ mV vs SCE}$ . The formulation consisting of 250 ppm DTPMP + 50 ppm  $\text{Ni}^{2+}$  shifts the corrosion potential to  $-765 \text{ mV vs SCE}$ . It shows that the corrosion potential is shifted to negative side. This suggests that the cathodic reaction is controlled predominantly.

The corrosion current density value and LPR value for sea water are  $6.351 \times 10^{-6} \text{ A cm}^{-2}$  and  $6.356 \times 10^3 \text{ ohm cm}^2$ . For the formulation of 250 ppm of DTPMP and 50 ppm of  $\text{Ni}^{2+}$ , the corrosion current density value has decreased to  $5.238 \times 10^{-6} \text{ A cm}^{-2}$  and the LPR value has increased to  $7.148 \times 10^3 \text{ ohm cm}^2$ . The fact that the LPR value increases with decrease in corrosion current density indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate with the formation of a protective film on the metal surface.

### AC impedance spectra

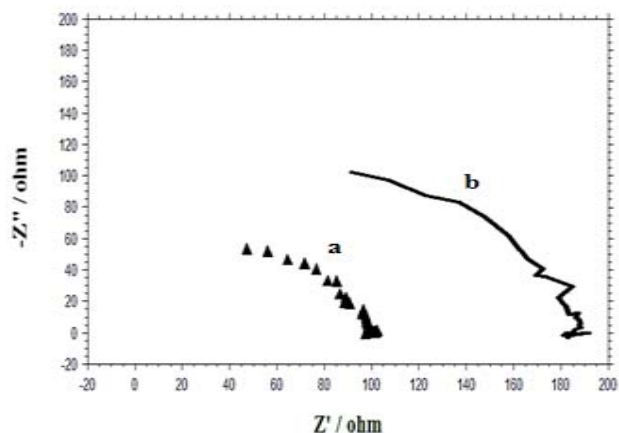
AC impedance spectra [electrochemical impedance spectra] have been used to confirm the formation of protective film on the metal surface.<sup>23-26</sup> The AC impedance spectra of carbon steel immersed in sea water in the absence and presence of inhibitors are shown in Fig.2 (Nyquist plots) and Fig.3 (Bode plots). The impedance parameters namely charge transfer resistance ( $R_t$ ), double layer capacitance ( $C_{dl}$ ), and impedance  $\lg(Z/\text{ohm})$  are given in Table 4. If a protective film is formed on the metal surface,  $R_t$  value increases and the  $C_{dl}$  value decreases.

**Table 4.** The AC impedance spectra of carbon steel immersed in sea water in presence of the inhibitor system

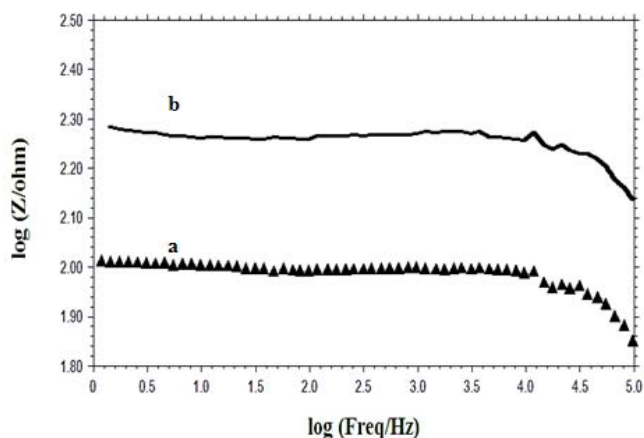
System	$R_t, \Omega \text{ cm}^2$	$C_{dl}, \text{F cm}^{-2}$	$\lg(Z \text{ ohm}^{-1})$
Sea water	$5.426 \times 10^1$	$9.3918 \times 10^{-8}$	2.010
Sea water + DTPMP (250 ppm) + $\text{Ni}^{2+}$ (50 ppm)	$2.0915 \times 10^2$	$2.4365 \times 10^{-8}$	2.282

When carbon steel is immersed in sea water,  $R_t$  value is  $5.426 \times 10^1 \Omega \text{ cm}^2$  and  $C_{dl}$  value is  $9.3918 \times 10^{-8} \text{ F cm}^{-2}$ . When DTPMP and  $\text{Ni}^{2+}$  are added to sea water,  $R_t$  value increases from  $5.426 \times 10^1 \Omega \text{ cm}^2$  to  $2.0915 \times 10^2 \Omega \text{ cm}^2$  and the  $C_{dl}$  value decreases from  $9.3918 \times 10^{-8} \text{ F cm}^{-2}$  to  $2.4365 \times 10^{-8} \text{ F cm}^{-2}$ . The impedance value increases from 2.010 to 2.282. This accounts for the high IE of DTPMP and  $\text{Ni}^{2+}$  system and a protective film is formed on the metal surface.

In electrochemical studies, instantaneous corrosion rates are measured. But in weight-loss method, corrosion rate is measured after a longer period, in the present study after one day. After a longer period, the protective film becomes more compact and stable. This accounts for the discrepancy in  $IE$ , obtained from AC impedance spectra and from weight-loss method.



**Figure 2.** AC impedance spectra (Nyquist plots) of carbon steel immersed in various test solutions **a)** sea water **b)** sea water containing 250 ppm of DTPMP and 50 ppm of  $Ni^{2+}$

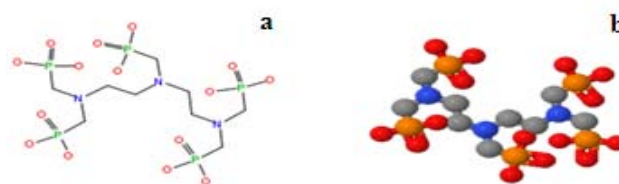


**Figure 3.** AC impedance spectra (Bode plots) of carbon steel immersed in various test solutions **a)** sea water **b)** sea water containing 250 ppm of DTPMP and 50 ppm of  $Ni^{2+}$

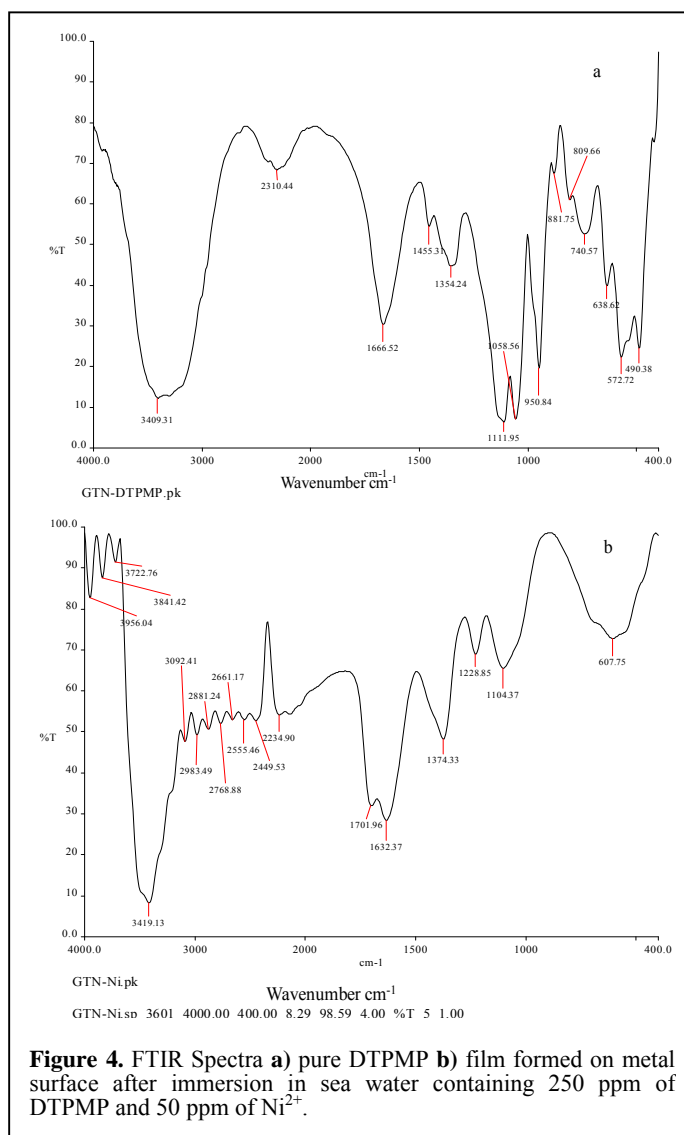
### FTIR Spectra

The structure of DTPMP is shown in Scheme 1. FTIR spectra have been used to analyse the protective film found on the metal surface.<sup>27,28</sup> The FTIR spectrum (KBr) of pure DTPMP is shown in Fig. 4a. The P-O stretching frequency appears at  $1058\text{ cm}^{-1}$  and the C-N stretching frequency appears at  $1111\text{ cm}^{-1}$ . The FTIR spectrum of the film formed on the metal surface after immersion in sea water containing 250 ppm of DTPMP and 50 ppm of  $Ni^{2+}$  is shown in Fig. 4b. The P-O stretching frequency has shifted from  $1058$  to  $1104\text{ cm}^{-1}$  and the C-N stretching frequency has shifted from  $1111\text{ cm}^{-1}$  to  $1228\text{ cm}^{-1}$ . The shift indicates that the oxygen and nitrogen atoms of phosphonic acid are coordinated to form  $Fe^{2+}$  - DTPMP complex on the anodic sites of the metal surface. The peak at  $3419\text{ cm}^{-1}$  is due to  $-OH$  stretching. The band due to Ni-O appears at  $1374\text{ cm}^{-1}$ . These results confirm the presence of  $Ni(OH)_2$  deposited on the cathodic sites of the metal surface. Thus, FTIR spectral study leads to

the conclusion that the protective film consists of  $Fe^{2+}$  - DTPMP complex and  $Ni(OH)_2$ .



**Scheme 1.** (a) 2D Structure of DTPMP (b) 3D Structure of DTPMP



**Figure 4.** FTIR Spectra **a)** pure DTPMP **b)** film formed on metal surface after immersion in sea water containing 250 ppm of DTPMP and 50 ppm of  $Ni^{2+}$ .

### Atomic Force Microscopy

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces.<sup>29</sup> AFM is becoming an accepted method for roughness investigation.<sup>30</sup> All atomic force microscopy images were obtained on PicoSPM Molecular Imaging, USA make, AFM instrument operating in contact mode in air. The scan size of all the AFM images are  $30\mu\text{m} \times 30\mu\text{m}$  areas at a scan rate of 2.4 lines per second. The two dimensional, three dimensional AFM morphologies and the AFM cross sectional profile for polished carbon steel surface (reference

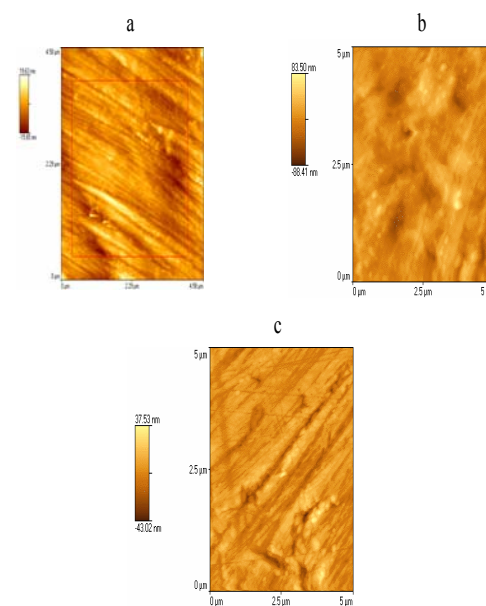
sample), carbon steel surface immersed in sea water (blank sample), and carbon steel surface immersed in sea water containing 250 ppm DTPMP and 50 ppm  $\text{Ni}^{2+}$  are shown in Fig.5 (a,d,g), (b,e,h), (c,f,i) respectively.

Root Mean Square Roughness, Average Roughness and Peak-to-Valley Value: AFM image analysis was performed to obtain the average roughness,  $R_a$  (the average deviation of all points roughness profile from a mean line over the evaluation length), root – mean – square roughness,  $R_q$  (the average of the measured height deviations taken within the evaluation length and measured from the mean line), and the maximum peak-to-valley ( $P-V$ ) height values (largest single peak-to-valley height in five adjoining sampling heights).<sup>30</sup>  $R_q$  is much more sensitive than  $R_a$  to large and small height deviations from the mean.<sup>31</sup>

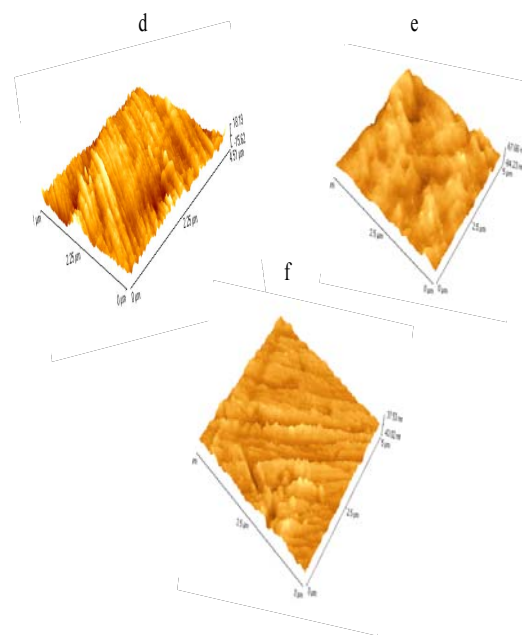
**Table 5.** AFM data for carbon steel immersed in inhibited and uninhibited environments.

Samples	$R_q$ , nm	$R_a$ , nm	$P-V$ , nm
Polished carbon steel, control	4.33	3.41	35.28
Carbon steel immersed in sea water (blank)	17.67	13.51	71.08
Carbon steel immersed in sea water containing 250 ppm DTPMP and 50 ppm $\text{Ni}^{2+}$	11.22	8.76	42.00

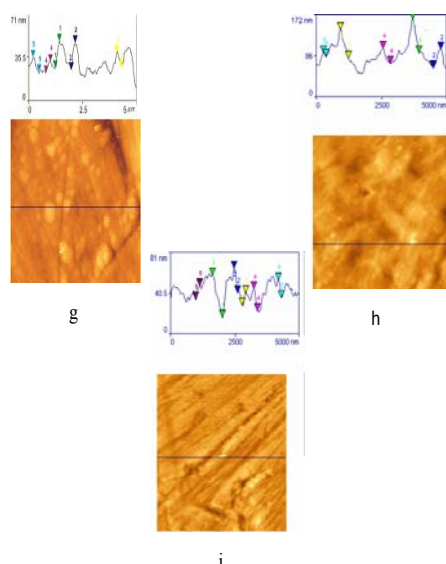
Table 5 is a summary of the average roughness ( $R_a$ ), rms roughness ( $R_q$ ), maximum peak to valley height ( $P-V$ ) value for carbon steel surface immersed in different environments. The value of  $R_q$ ,  $R_a$ , and  $P-V$  height for the polished carbon steel surface (reference sample) are 4.33 nm, 3.41 nm, and 35.28 nm respectively. This shows that the surface is more homogenous, with some places where the height is lower than the average depth. Fig. 5 (a,d,g) displays the non-corroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. Fig. 5 (b,e,h) displays corroded metal surface with few pits. The rms roughness, average roughness, and  $P-V$  height values for the carbon steel surface immersed in sea water are 17.67 nm, 13.51 nm, and 71.08 nm respectively. These values suggest that carbon steel surface immersed in sea water has a greater surface roughness than the polished metal surface, indicating that the unprotected carbon steel surface is rougher and were due to the corrosion of carbon steel in sea water environment. Fig. 5 (c,f,i) shows the carbon steel surface after immersion in sea water containing 250 ppm of DTPMP + 50 ppm  $\text{Ni}^{2+}$ . The  $R_q$ ,  $R_a$ , and  $P-V$  height values for carbon steel surface are 11.22 nm, 8.76 nm, and 42 nm respectively. These values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of  $\text{Fe}^{2+}$ -DTPMP complex and  $\text{Ni}(\text{OH})_2$  on the metal surface, thereby inhibiting the corrosion of carbon steel. The above parameters are also somewhat greater than the AFM data of polished metal surface, which confirms the formation of film on the metal surface, which is protective in nature.



**Figure 5.** Two dimensional AFM images of the surface of,  
 a) Polished carbon steel (control);  
 b) Carbon steel immersed in sea water (blank);  
 c) Carbon steel immersed in sea water containing DTPMP (250 ppm) +  $\text{Ni}^{2+}$  (50 ppm).



**Figure 5.** Three dimensional AFM images of the surface of,  
 d) Polished carbon steel (control);  
 e) Steel immersed in sea water (blank);  
 f) Carbon steel immersed in sea water containing DTPMP (250 ppm) +  $\text{Ni}^{2+}$  (50 ppm).



**Figure 5.** AFM cross-sectional images of the surface of,  
 (g) Polished carbon steel (control);  
 (h) Carbon steel immersed in sea water (blank);  
 (i) Carbon steel immersed in sea water containing DTPMP (250 ppm) + Ni<sup>2+</sup> (50 ppm).

#### Mechanism of corrosion inhibition

In order to explain the above results, the following mechanism of corrosion inhibition is proposed: When carbon steel is immersed in an aqueous solution, the anodic reaction is,

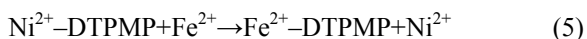


The corresponding cathodic reaction is reduction of oxygen to hydroxyl ions,



When the formulation consists of 250 ppm of DTPMP and 50 ppm Ni<sup>2+</sup> in sea water, there is formation of DTPMP–Ni<sup>2+</sup> complex in solution.

When carbon steel is immersed in this environment, the DTPMP–Ni<sup>2+</sup> complex diffuses from the bulk of the solution to the metal surface. The DTPMP–Ni<sup>2+</sup> complex is converted into DTPMP–Fe<sup>2+</sup> complex on the anodic sites of the metal surface, the stability of Fe<sup>2+</sup>–DTPMP complex is higher than the corresponding Ni complex.



The released Ni<sup>2+</sup> combines with OH<sup>-</sup> to form Ni(OH)<sub>2</sub> on the cathodic sites of the metal surface.



The protective nature of the film is due to the presence of metal inhibitor complex and nickel hydroxide. Formation of the metal inhibitor complex fills the pores of the otherwise porous film and makes it a protective film.

Thus, the protective film consists of Fe<sup>2+</sup> – DTPMP complex and Ni(OH)<sub>2</sub>.

## CONCLUSIONS

The conclusions drawn from the results may be given as: The formulation consists of 250 ppm of DTPMP and 50 ppm of Ni<sup>2+</sup> has 70 % IE. Polarization study suggests that the cathodic reaction is controlled predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra show that the protective film consists of Fe<sup>2+</sup>–DTPMP complex and Ni(OH)<sub>2</sub>. AFM images confirm the formation of protective layer on the metal surface.

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