



Corrosion Inhibition by Sodium Gluconate-Zn²⁺-DTPMP System

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Abstract: The inhibition efficiency of a phosphonic acid, Diethylene Triamine Pentamethylene Phosphonic acid (DTPMP) in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl⁻ has been evaluated by weight loss method in the absence and presence of Zn²⁺. The formulation consisting of DTPMP and Zn²⁺ has excellent inhibition efficiency (IE). A synergistic effect is noticed between Zn²⁺ and DTPMP. Addition of sodium gluconate (SG) enhances the IE of Zn²⁺ and DTPMP system. The DTPMP-Zn²⁺-SG system function as a mixed inhibitor as revealed by polarization study. AC impedance spectrum, optical and atomic force micrographs reveal the formation of a protective film on the metal surface. FTIR spectra reveal that the protective film consists of Fe²⁺-DTPMP complex, Fe²⁺-SG complex and Zn(OH)₂.

Keywords: Corrosion inhibition, Carbon steel, Phosphonic acid, Atomic force microscopy.

Introduction

Several phosphonic acids have been used as corrosion inhibitors due to their ability to form complexes with metal ions and hydrolytic stability¹⁻¹⁵. Phosphonic acids such as phenyl phosphonic^{9,13} 1-hydroxyethane-1,1-diphosphonic acid^{11,12}, ethylphosphonic acid and 2-chloroethyl phosphonic acid¹⁶ have been used as corrosion inhibitors. The present work is undertaken:

- i) To evaluate the IE of the DTPMP-Zn²⁺ system in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of Cl⁻.
- ii) To investigate the influence of sodium gluconate on the IE of DTPMP-Zn²⁺ system.
- iii) To study the mechanistic aspects of corrosion inhibition by polarization and AC impedance method.
- iv) To analyze the protective film by FTIR, and atomic force micrographs.
- v) To propose a suitable mechanism of corrosion inhibition based on the results obtained from the above methods.

Experimental

These studies are confined to a single metal species that is carbon steel of composition:

Elements	C	Mn	P	Si	S	Cr	Ni	Mo	Fe
Composition %	0.098	0.179	0.012	0.024	0.01	0.0023	0.018	<0.001	99.57

The presence of the above elements in the mild steel was analyzed using vacuum emission spectrometer DV-4 (supplied by BAIRD Corporation). Mild steel specimens of the dimensions 1.0×4.0×0.2 cm were polished to mirror finish using emery sheets, (No.0/2, 0/3), washed with double distilled water, degreased with trichloroethylene, dried and used for the weight loss method and surface examination studies. The specimens were stored in a desiccator and used for all investigations. Carbon steel rod encapsulated in Teflon with an exposed cross section of 1 cm² diameter was used as the working electrode in potentiostatic polarisation and AC impedance studies.

Weight loss method

The mild steel specimens were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn²⁺, for a period of 3 days. The weights of the specimens before and after immersion were determined using Metler balance-AE-240. The corrosion products were cleaned. The percent inhibition efficiency (IE) was calculated using the relation

IE = [(W₁-W₂)/W₁]×100, where W₁ and W₂ are weight losses of mild steel in uninhibited and inhibited chloride solutions.

Potentiostatic polarization study / AC impedance spectra

The measurements were carried using corrosion measurement system (EG & G Electrochemical Impedance Analyzer Model 6310) provided with a rectangular specimen of carbon steel as working electrode, platinum foil as the counter electrode and saturated calomel electrode as reference electrode. The reference electrode was placed close to the working electrode to minimize IR contribution. A time interval of about 5 to 10 min was given for the working electrode to attain a steady state open circuit potential.

Surface examination study

FTIR spectra

The surface film was scratched carefully and the powder obtained was thoroughly mixed so as to make it uniform throughout. The FTIR spectra of the powder (KBr pellet) were recorded in Perkin Elmer-1600 spectrometer.

Surface morphology

Atomic Force Microscope is used for surface morphology studies. Atomic force microscope (AFM) is an exciting new technique that allows surface to be imaged at higher resolutions and accuracies than ever before. The protective films are examined for a scanned area of 5×5 μm are evaluated for a set point of 10 nA and a scan speed of 10 mm/s. The three and two dimensional topography of surface films gave various roughness parameters of the film. AFM makes 3-D images of the surfaces by a tiny stylus gently contacts the specimen. As the XYZ translator scans either the specimen or the stylus horizontally in a raster pattern (XY), the stylus rides up and down the surface hills and valleys. The laser sensor and the XYZ register the deflection of the stylus and the XYZ translator adjusts specimen up and down (Z). The computer stores the vertical position at each point and assembles the image.

Results and Discussion

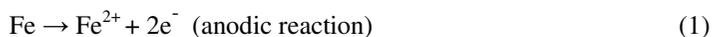
The inhibition efficiencies (IE) of DTPMP in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl⁻, in the absence and presence of Zn²⁺ are given in Table 1.

Table 1. Inhibition efficiency (%) offered by the inhibitor system to carbon steel immersed in 60 ppm of Cl⁻ system.

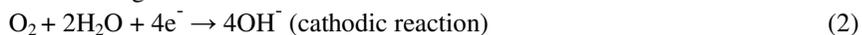
Inhibitor system: DTPMP+Zn²⁺ Immersion period: 3 days pH = 7

DTPMP ppm	Zn ²⁺ , ppm		
	0	10	25
0	-	15	5
50	11	-30	98
100	15	-25	95
150	21	-12	70
200	24	-3	68
250	28	20	64

It is found that DTPMP shows some IE. When 10 ppm of Zn²⁺ is added, the IE decreases. There is acceleration of corrosion. This is due to the fact that at this lower concentration of Zn²⁺, DTPMP is precipitated as Zn²⁺-DTPMP complex in the bulk of the solution. DTPMP is not transported towards the metal surface. However when 25 ppm of Zn²⁺ is added, the IE of DTPMP increases tremendously. A synergistic effect is noticed between DTPMP and Zn²⁺. For example 25 ppm of Zn²⁺ has only 5% IE and 50 ppm of DTPMP has 50% IE. But their combination has 98% IE. This may be explained as follows: when 25 ppm of Zn²⁺ is added to DTPMP, Zn²⁺-DTPMP complex is in solubilised form. It diffuses towards the metal surface. On the anodic site Fe²⁺-DTPMP complex is formed. Zn²⁺ is released which combines with OH⁻ generated by cathodic reaction. Thus the anodic reaction of the formation of Fe²⁺



and cathodic reaction of generation of OH⁻



are controlled by the Zn²⁺-DTPMP system. This accounts for the synergistic effect.

Influence of sodium gluconate (SG) on Zn²⁺-DTPMP system

The formulation consisting of 10 ppm Zn²⁺ and 100 ppm DTPMP is found to be corrosive (-25%) (Table 2).

Table 2. Influence of sodium gluconate (SG) on the IE of the DTPMP-Zn²⁺ system.

Inhibitor system: DTPMP+Zn²⁺+SG Immersion period: 3 days pH= 7

Zn ²⁺ , ppm	DTPMP, ppm	SG, ppm	Corrosion rate, mdd	IE, %
10	100	0	22.5	-25
10	100	50	10.6	41
10	100	100	9.7	46
10	100	150	4.7	74
10	100	200	4.0	78
10	100	250	3.60	80

But when SG is added, the IE increases. As the concentration of SG increases, IE also increases. The anodic reaction is controlled by the formation of Fe^{2+} -DTPMP complex and Fe^{2+} -SG complex on the sites of the metal surface. The cathodic reaction is controlled by the formation of $\text{Zn}(\text{OH})_2$ on the cathodic sites of the metal surface.

Influence of pH on the DTPMP-SG system

The influence of pH on the DTPMP- Zn^{2+} -SG system is given in Table 2 to 5.

Table 3. Corrosion rates of carbon steel in aqueous environment ($\text{Cl}^- = 60$ ppm), in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method

Inhibitor system: DTPMP + Zn^{2+} SG Immersion period=3 days pH=5					
S. No.	DTPMP, ppm	Zn^{2+} , ppm	SG, ppm	Corrosion rate, mdd	IE, %
1	0	0	0	20.33	---
2	100	10	50	45.74	-125
3	100	10	100	39.24	-93
4	100	10	150	37.61	-85
5	100	10	200	34.76	-71
6	100	10	250	31.11	-53

Table 4. Corrosion rates of carbon steel in aqueous environment ($\text{Cl}^- = 60$ ppm), in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method.

Inhibitor system: DTPMP + Zn^{2+} SG Immersion period=3 days pH=8					
S. No.	DTPMP, ppm	Zn^{2+} , ppm	SG, ppm	Corrosion Rate, mdd	IE, %
1	0	0	0	16.33	---
2	100	10	50	41.64	-155
3	100	10	100	38.38	-135
4	100	10	150	35.93	-120
5	100	10	200	34.95	-114
6	100	10	250	34.62	-112

Table 5. Corrosion rates of carbon steel in aqueous environment ($\text{Cl}^- = 60$ ppm), in the presence and absence of inhibitor and the inhibition efficiencies obtained by the weight loss method.

Inhibitor system: DTPMP + Zn^{2+} SG Immersion period =3 days pH=10					
S. No.	DTPMP, ppm	Zn^{2+} , ppm	SG, ppm	Corrosion rate, mdd	IE, %
1	0	0	0	15.67	---
2	100	10	50	43.41	-177
3	100	10	100	40.74	-160
4	100	10	150	36.04	-130
5	100	10	200	35.26	-125
6	100	10	250	34.32	-119

It is seen from Table 3 that when the pH is changed from 7 to 5 (addition of dil H_2SO_4) the inhibition efficiency is altered very much. For example the system consist of 100 ppm DTPMP, 10 ppm of Zn^{2+} and 250 ppm of SG has 80% IE at pH 7 is reduced to 53% at pH 5. When the pH is increased from 7 to 8 then to 10 (addition of dil NaOH) the IE is very much

lowered, that is from 80% to -112% and to -119% respectively for the above said formulation. This is due to the fact that at pH 8 and 10 when NaOH is added, Zn²⁺ is precipitated as Zn(OH)₂. Hence Zn²⁺ is not transported from the bulk of the solutions to the metal surface. Hence the analysis shows that in acidic and alkaline medium SG does not show good IE.

Potentiostatic polarization study

The corrosion parameters of carbon in various test solutions are given Table 6.

Table 6. Corrosion parameters of carbon steel immersed in chloride environment obtained by polarization method.

Inhibitor system: DTPMP + Zn ²⁺ + SG							Immersion period = 3 days	pH=7
DTPMP, ppm	SG ppm	Zn ²⁺ ppm	E _{corr.} mV vs. SCE	b _c mV	b _a mV	I _{corr.} A/cm ²		
60	0	0	-402	100	118	6.4938×10 ⁻⁶		
60	100	100	-392	95	100	4.8696×10 ⁻⁶		

The polarization curves are shown in Figure 1.

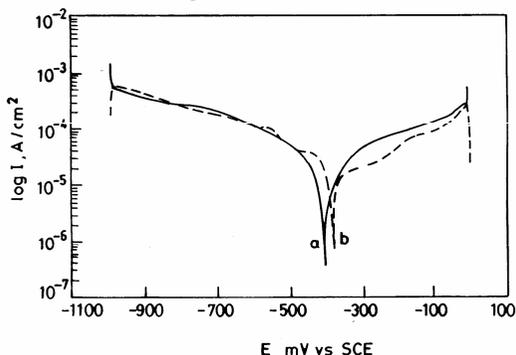


Figure 1. Potentiostatic polarization curves of carbon steel immersed in various test solutions. [(a) Cl⁻ 60 ppm (b) Cl⁻ 60 ppm+10 ppm Zn²⁺+100 ppm DTPMP+100 ppm SG].

When carbon steel is immersed in aqueous solution containing 60 ppm Cl⁻, the corrosion potential is -402 mV vs. SCE. When inhibitors namely, DTPMP, SG and Zn²⁺ are added, the corrosion potential is shifted to anodic side (-392 mV vs. SCE). This suggests that this formulation controls anodic reaction predominantly. The Tafel slopes are almost equal (b_c = 95 mV; b_a=100 mV). This suggests that this formulation function as a mixed inhibitor, controlling anodic reaction and cathodic reaction almost equally.

Analysis of the results of AC impedance spectra

The A.C. impedance parameters of carbon steel immersed in various test solutions are given Table 7.

Table 7. AC impedance parameters of carbon steel immersed in chloride environment

Inhibition system: DTPMP+Zn ²⁺ SG					Immersion period = 3days	pH = 7
Cl ⁻ ppm	DTPMP ppm	SG, ppm	Zn ²⁺ , ppm	Rt Ω cm ²	Cdl, μF/cm ²	
60	0	0	0	62.6	1.606×10 ⁻⁴	
60	100	100	10	165.6	0.06067×10 ⁻⁴	

The spectra are shown in Figure 2.

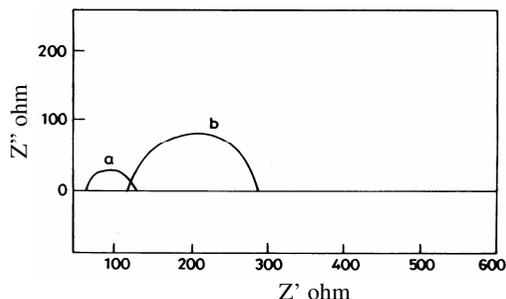


Figure 2. A.C. impedance curves of carbon steel immersed in various test solutions.

[(a) Cl^- 60 ppm (b) Cl^- 60 ppm + 10 ppm Zn^{2+} + 100 ppm DTPMP + 100 ppm SG]

When the inhibitors namely, DTPMP, SG and Zn^{2+} are added, the charge transfer resistance R_t increases from 62.6 ohm cm^2 to 165.6 ohm cm^2 ; the double layer capacitance C_{dl} decreases from $1.606 \times 10^{-4} \mu\text{F/cm}^2$ to $0.06067 \times 10^{-4} \mu\text{F/cm}^2$. Thus A.C. impedance spectra reveal that a protective film is formed on the metal surface

Analysis of FTIR spectra

The FTIR spectrum of pure DTPMP is shown in Figure 3a. The P-O stretching frequency appears at 1059 cm^{-1} . The C-N stretching frequency appears at 1111 cm^{-1} . The P-OH group causes absorption at 3000 cm^{-1} and P(O)(OH) group at 3433 cm^{-1} . The absorption band at 1059 cm^{-1} represents P-O stretching frequency. The absorption at 1344 cm^{-1} represent P=O stretching. The absorption bands due to the bending of O-P-O appear at 490 cm^{-1} , 575 cm^{-1} and 640 cm^{-1} . The bending vibration ($\delta_s \text{ CH}_2$ scissoring) of aliphatic tertiary amine group $\text{CH}_2\text{N-}$ appears at 1458 cm^{-1} . The weak C-C stretching vibration appears at 951 cm^{-1} , 881 cm^{-1} and 737 cm^{-1} . The aliphatic $-\text{CH}_2$ group appears at 2927 cm^{-1} . The absorption at 1406.25 cm^{-1} results from the $-\text{CH}_2$ group absorption of $-\text{CH}_2\text{-P}$. Thus diethylene triamine pentamethylene phosphonic acid with molecular formula $\text{C}_9\text{H}_{28}\text{N}_3\text{O}_{15}\text{P}_5$ is characterized by the FTIR spectrum. The FTIR spectrum of pure Sodium gluconate (SG) is shown in Figure 3b. The C=O stretching frequency appears at 1595 cm^{-1} .

Analysis of FTIR spectra

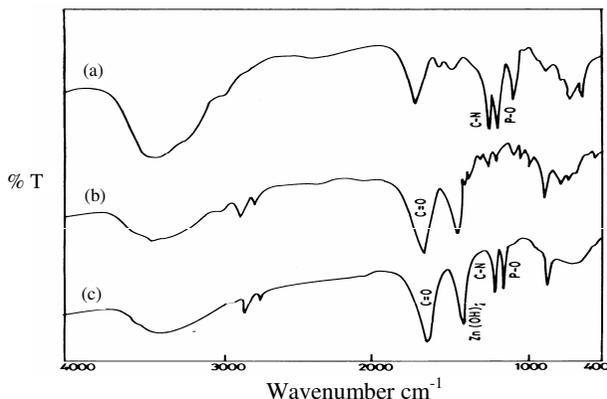


Figure 3. FTIR spectra of DTPMP (a) and carbon steel immersed in various test solutions (b) and (c); [(a) Pure DTPMP; (b) Cl^- 60 ppm + 10 ppm Zn^{2+} + 100 ppm DTPMP; (c) Cl^- 60 ppm + 10 ppm Zn^{2+} + 100 ppm DTPMP + 100 ppm SG].

The FTIR spectrum of the film (KBr) formed on the surface of carbon steel after immersion in the test solution containing DTPMP, SG and Zn²⁺ is shown in Figure 3c. The C-N stretching frequency has shifted from 1111 cm⁻¹ to 1126 cm⁻¹. The P-O stretching frequency has shifted¹⁷⁻¹⁹ from 1059 cm⁻¹ to 1032 cm⁻¹.

The C=O stretching frequency of SG has shifted from 1595 cm⁻¹ to 1590 cm⁻¹. This suggests the formation of Fe²⁺-DTPMP complex and also Fe²⁺-SG complex on the metal surface. DTPMP has coordinated with Fe²⁺ through N and O atoms of phosphonic acid. SG has coordinated with Fe²⁺ through O atom of carboxyl group. The peak²⁰ at 1350 cm⁻¹ is due to Zn (OH)₂.

Table 8. Summary of FTIR spectral analysis¹⁷⁻²⁰.

S. No.	System	Prominent peaks, cm ⁻¹	Inference
1	100 ppm of DTPMP, Figure 3a	1059	P-O stretching frequency
2	"	1111	C-N stretching frequency
3	"	3000	P-OH absorption frequency
4	"	3433	P (O)(OH)
5	"	1344	P=O
6	"	490, 575, 640	O-P-O bending frequency
7	"	1458	δ _s CH ₂ (scissoring)
8	"	951, 881, 737	Weak C-C stretching frequency
9	"	2927	Aliphatic CH ₂ gp
10	"	1406	-CH ₂ absorption frequency of -CH ₂ -P< gp
11	Sodium Gluconate, Figure 3b	1595	C=O stretching frequency
12	DTPMP+Zn ²⁺ +SG+ Cl ⁻ Figure 3c	1126	-CN Fe ²⁺ -DTPMP complex Fe ²⁺ -SG complex
13	"	1032	-P-O
14	"	1590	-C=O
15	"	1350	Zn(OH) ₂

Analysis of atomic force micrographs

The coated protective films are examined with Atomic Force Microscope (AFM). The topography of all the samples for a scanned area of 5 nm x 5 nm (25 nm²) is evaluated for a set point of 10 nA and a scan speed of 10 mm/s. The three dimensional (3D) images of topography in forward and reverse direction indicates the important parameters namely Roughness of metal surface (Rms) and Z_{max} voltage indicate the conducting feature of thin films on the metal surface.

The contact mode of operation used in this analysis is known as *constant force* enables a fairly faithful topographical image to be obtained (hence the alternative name, *height mode*). Height image data obtained by the AFM is three-dimensional. The usual method for displaying the data is to use a color mapping for height, for example Figure 4 black for low features and white for high features. Similar color mappings can be used for non-topographical information such as phase or potential.

The Table 9 shows various AFM parameters obtained when the carbon steel surface immersed in different environments. Figure 4(a) & (b) shows one and 3D AFM images of polished metal surface. Z_{max} value 0.51V when compared with other thin film coated surface values indicate the absence of iron oxides on the smooth surface. Figure 5(a)& (b) shows

one & 3-D images of polished metal surface immersed in 60 ppm Cl⁻ ion solution for 10 min indicate the formation of iron oxides by the increased Z_{max} value of 0.85 volts. Figure 6 (a)&(b) shows one and 3-D images of carbon steel immersed in 60 ppm Cl⁻+10 ppm Zn²⁺ solution in which increased Rms value 253 nm and Z_{max} value 0.78 V represent the formation of protective thin film on the metal surface.

Figure 7(a)& (b) shows one and 3-D images of carbon steel immersed in 60 ppm Cl⁻+10 ppm Zn²⁺+100 ppm DTPMP and 8(a) &(b) shows the one and 3-D images of carbon steel immersed in 60 ppm Cl⁻+10 ppm Zn²⁺+100 ppm DTPMP+100 ppm SG for 10 min duration respectively. When the immersion period is 10 min roughness value increases from 179.51 nm to 379 nm. These increased values strongly imply the formation of inhibitive film by the addition of SG additive along with the phosphonic acid inhibitor system on the metal surface.

Table 9. AFM parameters of carbon steel immersed in neutral aqueous environment

S.No.	Environment	Period of immersion	AFM parameters	
			Rms nm	Z _{max} volts
1.	Polished metal	-	143.98	0.51
2.	Polished metal + 60 ppm Cl ⁻	10 min.	148.83	0.85
3.	Polished metal + 60 ppm Cl ⁻ +10 ppm Zn ²⁺	10 min.	252.46	0.78
4.	Polished metal + 60 ppm Cl ⁻ +10 ppm Zn ²⁺ + 100 ppm DTPMP	10 min.	179.51	0.75
5.	Polished metal + 60 ppm Cl ⁻ +10 ppm Zn ²⁺ + 100 ppm DTPMP+100 ppm SG	10 min.	379.00	0.61

Atomic force micrographs of mild steel immersed in various inhibitor systems.

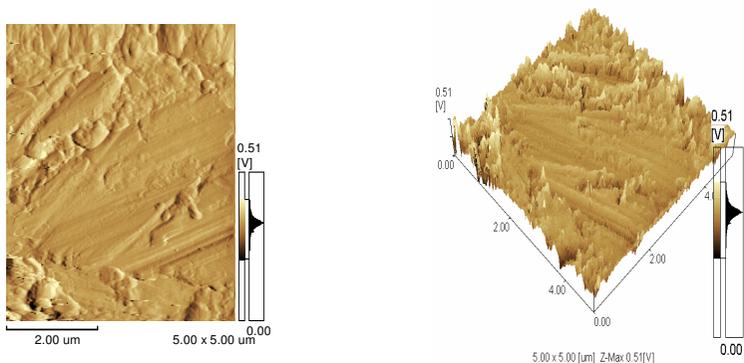


Figure 4(a). AFM image of polished mild steel surface.

Figure 4(b). AFM 3D image of polished mild steel surface

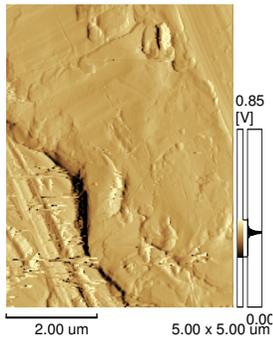


Figure 5(a). AFM image of polished steel surface immersed in 60 ppm Cl⁻ + Zn²⁺ system

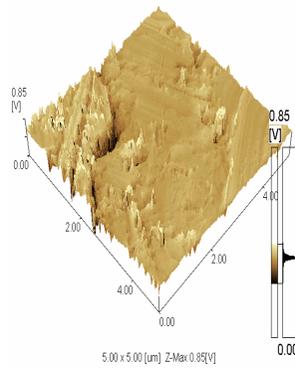


Figure 5(b). AFM 3D image of polished mild steel surface immersed in 60 ppm Cl⁻ + Zn²⁺ system

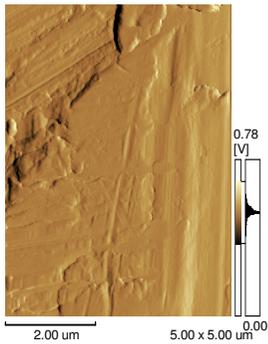


Figure 6(a). AFM image of Polished Mild steel surface immersed in Zn²⁺ system

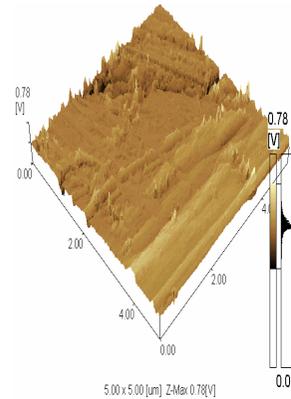


Figure 6(b). AFM 3D image of Mild steel surface immersed in Zn²⁺ system

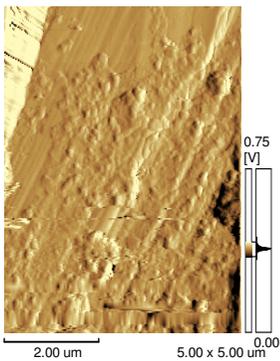


Figure 7(a). AFM image of Polished Mild steel surface immersed in Zn²⁺ + DTPMP system

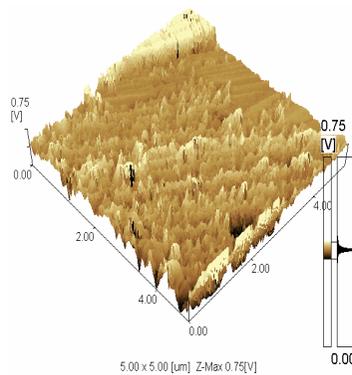


Figure 7(b). AFM 3D image of Mild steel surface immersed in Zn²⁺ + DTPMP system.

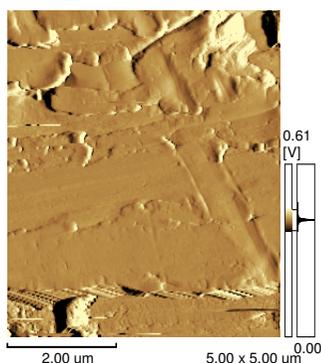


Figure 8(a). AFM image of Polished Polished Mild steel surface immersed Zn^{2+} +DTPMP+SG system

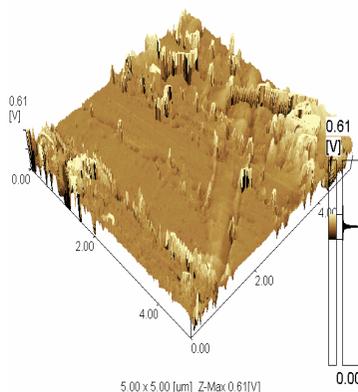


Figure 8(b). AFM 3D image of Mild steel surface immersed in Zn^{2+} + DTPMP + SG system

Mechanism of corrosion inhibition

Fe^{2+} -SG complex and $\text{Zn}(\text{OH})_2$. In order to explain these observations in a holistic way, the following mechanism of corrosion inhibition is proposed; the formulation consisting of 10 ppm of Zn^{2+} , 100 ppm of DTPMP and 100 ppm of SG has 46% IE. Polarization study reveals that this formulation functions as a mixed inhibitor. A.C. impedance spectra reveal the presence of a protective film on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+} -DTPMP complex,

- 1) When the formulation consisting of 60 ppm of Cl^- , 100 ppm of DTPMP, 10 ppm of Zn^{2+} and 100 ppm of SG is prepared, there is formation of Zn^{2+} -DTPMP complex and Zn^{2+} -SG complex in solution.
- 2) When carbon steel is immersed in this solution these complexes diffuse towards the metal surface.
- 3) On the metal surface the zinc complexes are converted into Iron complexes on the anodic sites. Zn^{2+} -DTPMP + Fe^{2+} -DTPMP + Zn^{2+} Zn^{2+} -SG + Fe^{2+} \rightarrow Fe^{2+} -SG + Zn^{2+} .
- 4) The released Zn^{2+} ions combine with OH^- ions forming $\text{Zn}(\text{OH})_2$ on the cathodic sites $\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2 \downarrow$.
- 5) Thus the protective film consists of Fe^{2+} -DTPMP complex, Fe^{2+} -SG complex and $\text{Zn}(\text{OH})_2$.

Conclusions

The corrosion rates of carbon steel immersed in Cl^- ion environment in the absence and presence of DTPMP and Zn^{2+} have been evaluated. The influence of sodium gluconate (SG) on the corrosion inhibition efficiency of DTPMP (Diethylene triamine pentamethylene phosphonic acid)- Zn^{2+} system has also been evaluated. The present study leads to the following conclusions:

- The weight loss results indicate that the formulation consisting of 10 ppm of Zn^{2+} , 100 ppm of DTPMP and 100 ppm of SG has 46% IE. As the concentration of SG increases, IE also increases.
- Influence of pH on the IE of this inhibitor system indicates that SG shows excellent IE in neutral aqueous medium.

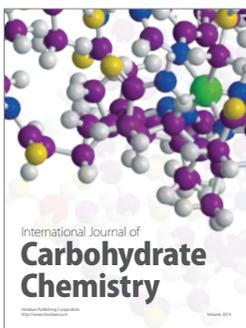
- Polarization study reveals that this formulation functions as a mixed inhibitor.
- A.C. impedance spectra reveal the presence of a protective film on the metal surface.
- FTIR spectral data appear to indicate that the protective film consists of Fe²⁺-DTPMP complex, Fe²⁺-SG complex and Zn (OH)₂.
- The protective film formation is also confirmed by Atomic force microscopic study.

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