Inhibitive action of DTPMP-SG-Zn^{2+} system in controlling Corrosion of Carbon steel in Neutral Aqueous Environment

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Abstract— **((Diethylenetriamine penta(methylene phosphonic acid (DTPMP) in the presence of Zn^{2+} ions are used to functions as the corrosion inhibitors in controlling the corrosion of carbon steel in 60 ppm Cl^-. To reduce the toxic nature of Zn^{2+} has to add other agents like Sodium Gluconate (SG). DTPMP is environment- friendly, non-toxic and non-polluting agent is used to control the rate of corrosion. Here, the corrosion control of carbon steel in 60 ppm Cl^- was investigated by Weight-loss study, electrochemical measurements and surface examination studies like FT-IR and SEM. The corrosion Inhibition Efficiency (IE) offered by 25 ppm of DTPMP, 25 ppm of SG, 10 ppm of Zn^{2+} was 96 %. The synergistic behaviour of inhibiting action was also found between the inhibitors. Electrochemical Impedance spectra indicates that surface film formed on the carbon steel shows that high charge transfer resistance and low Double layer capacitance, which suggests the film, is non-porous and protective. Potentiodynamic polarization study shows that the system works as an anodic inhibitor. The FT-IR spectra reveals that the protective film consists of Fe^{2+} - DTPMP complex, Fe^{2+} - SG complex and $Zn(OH)_2$ formation. The SEM micrograph shows that the protective film is formed on the metal surface.**

Keywords- Carbon steel; Phosphonic acid; Corrosion inhibition; F-Test; FT-IR spectra

I. INTRODUCTION

Water is the most commonly used cooling fluid to remove unwanted heat from heat transfer surfaces. If absolutely pure water was used in the cooling system, none of the problems would exist. Unfortunately, waters remain dissolved and suspended solids dissolved and suspended organic matters and dissolved gases. Finally in cooling water system, If the salt reaches their saturation point they may be thrown out in the form of precipitate may be called as scale [1]. Many inhibitors have been used in cooling water systems in order to solve these problems [2-4]. Particularly several phosphonic acids have been used as corrosion inhibitors due to their ability to from complexes with metal ions and hydrolytic stability [5]. DTPMP have been used as a corrosion inhibitors. The present work leads to evaluate the Inhibition efficiency (IE) of the DTPMP – SG – Zn^{2+} system in controlling the corrosion of carbon steel in 60 ppm Cl^- . To study the influence of Sodium gluconate (SG).To analyzes the protective film by FT-IR spectra. The polarization study reveals whether the system may functions as anodic or cathodic inhibitor

II. EXPERIMENTAL

A. Preparation of Carbon Steel specimen:

Carbon steel samples with the composition (C – 0.188% , S – 0.016 %, Si – 0.346 %, Mn – 1.15%, P – 0.036 %, Cr – 0.557%, Mo – 0.225 %, Ni – 0.0847%, Al – 0.0417%, Cu- 0.0342%, Ti- 0.0149%, V – 0.0313%, Pb- 0.0006% and rest Iron 97.27%) were used for weight-loss study and electrochemical measurements, specimen of the size 1.0 cm x 0.2 cm x 4.0 cm.

B. Weight – Loss Measurement

Carbon Steel specimen in Triplicate were immersed in 60 ppm Cl^- with and without inhibitor. After the immersion period is over specimens were taken out, rinsed in running tap water and kept in a desiccators. The corrosion products was cleaned with Clark's solution [6]. Then Weight – loss determined in order to calculate the Inhibition Efficiency and Corrosion Rate (CR) using the following formulae. The synergism parameter can be calculated by using the equation indicated the synergistic effect existing between the inhibitors [7]. SI value is found to be greater than one suggesting that the synergistic effect between the inhibitors.

$$W_o – W_i$$

$$I\,E = \frac{\quad}{W_o} \times 100$$

Where, W_o = Weight – loss in absence of an inhibitor, W_i = Weight – loss in presence of an inhibitor

$$CR = \frac{534 \times \text{Loss in Weight (mg)}}{D\,(g/cm^3) \times A\,(in^2) \times T\,(Hrs)}\ (mpy)$$

D – Density of the metal specimen (g/cm^3), A – Area of the specimen in in^2, T – Immersion time in Hours

C. Electrichemical Impedance Spectra

The electrochemical measurements presented in this study were performed using the Electrochemical Workstation (Model No. CHI760, CH Instruments, USA). Prior to the electrochemical measurements, the metal specimens were prepared according to the above described procedure.

D. Surface Examination studies

The carbon steel specimens were immersed in blank as well as inhibitor solutions, for a period of 3 days. After the immersion period is over, the specimens were taken out and dried. The nature of the thin film formed on the surface of the metal specimens was analyzed by various surface analysis techniques. The FT-IR and SEM used to give the information about the surface.

III. RESULTS AND DISCUSSION

A. Weight – Loss method : Inhibition Efficiency and Corrosion rate for the inhibitor formulation in neutral aqueous medium

The inhibition efficiency (IE) and Corrosion rate (CR) of Sodium Gluconate (SG) in corrosion control of carbon steel immersed in 60 ppm Cl^- for a period of three days. In the absence and the presence of Zn^{2+} is also studied which is given in Table 1. The lower corrosion inhibition takes place in the absence of SG. When SG is combined with Zn^{2+} ions increases the inhibition efficiency. For example, 25 ppm SG has only 15 % IE and 10 ppm Zn^{2+} has only 24 %, interestingly, their combination shows 53 % IE. This suggests a synergistic effect between the binary inhibitor formulation SG and Zn^{2+} ions. In order to improve the inhibition efficiency of DTPMP in ternary inhibitor formulation, experiments were conducted with DTPMP alone, SG and with Zn^{2+} with the wide range of concentration of DTPMP. The highest inhibition efficiency with these systems is 96%. The Inhibitor formulation consists of 25 ppm SG + 25 ppm DTPMP + 10 ppm Zn^{2+} gives the maximum IE. When SI > 1, this points to the synergistic effect. In the case of SI < 1, the negative interaction of inhibitors prevails (Increase in corrosion rate taking place) [8]. From Table 1 the most values are greater than unity, suggesting that the synergistic behavior is existing between the inhibitors.

TABLE 1. INHIBITION EFFICIENCIES (IE) OF CARBON STEEL IN 60 PPM Cl^-, THE ABSENCE AND THE PRESENCE OF INHIBITORS AND INHIBITION EFFICIENCY (IE) OBTAINED BY WEIGHT – LOSS METHOD AND SYNERGISM PARAMETER

SG [ppm]	**Zn^{2+}[ppm]**	**DTPM [ppm]**	**Corrosion Rate [mpy]**	**IE %**
25	0	0	1.50	15
0	10	0	1.34	24
0	0	25	1.60	10
25	10	0	0.82	53
0	10	25	1.13	36
25	10	5	0.80	55
25	10	10	0.37	79
25	10	25	0.07	96
25	10	50	0.25	85
25	10	75	0.30	83
SG +Zn^{2+} [I_2] IE %		DTPMP [I_1] IE %	SG-Zn^{2+} - DTPMP [I'_{1+2}] IE %	SI
53		15	55	13.48
53		25	79	16.00
53		10	96	4.92
53		22	85	13.00
53		27	83	16.48

B. Analysis of FT-IR Spectra

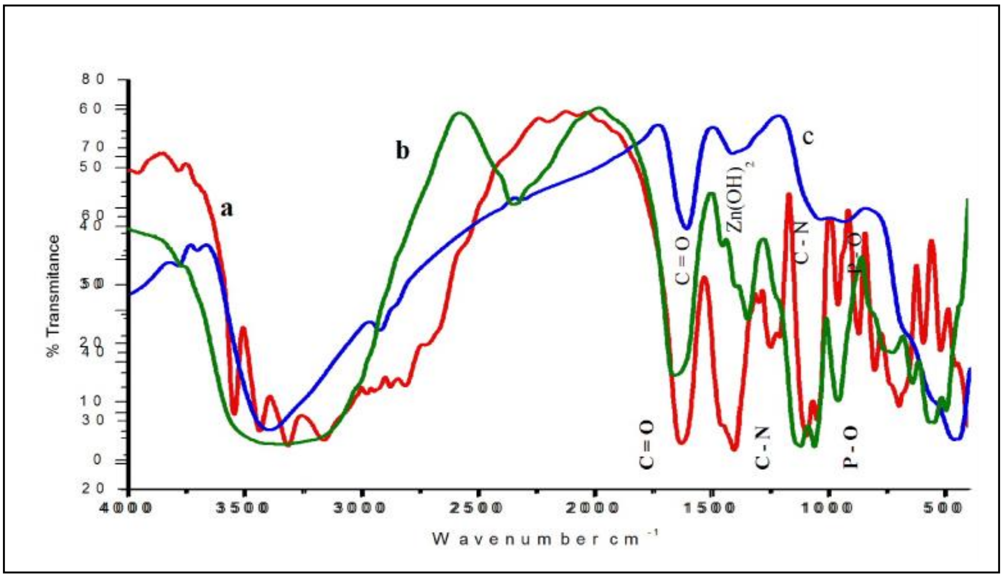


Figure.1 a, b, c is shown FT- IR spectra

Figure.1. a) Pure SG Figure.1. b) Pure DTPMP Figure.1. c) Film formed on the metal contains 25ppm DTPMP + 25 ppm SG + 10 ppm Zn^{2+}

The FT-IR spectrum of pure DTPMP is shown in **Fig. 1. (b)** . The P – O stretching frequency appears at 1059 cm^{-1}. The C – N Stretching frequency appears at 1116 cm^{-1}. P- OH group causes absorption at 3332 cm^{-1} and P(O) OH group at 3402 cm^{-1}. The absorption band at 1059 cm^{-1} represents P – O stretching frequency. The absorption band at 1346 cm^{-1} represent P = O stretching. Thus DTPMP with molecular formula $C_9H_{28}N_3O_{15}P_5$ is characterized by FT-IR spectrum. The FT-IR spectrum of the film (KBr) formed on the surface of carbon steel after immersion in the test solution containing 25 ppm DTPMP, 25 ppm SG and 10 ppm of Zn^{2+} is shown in the **Fig.1.(c)**.The C-N stretching frequency has shifted from 1116 cm^{-1} to 1043 cm^{-1}. The P – O stretching frequency has shifted from 1059 cm^{-1} to 945 cm^{-1}. The FT-IR spectrum of pure SG shown in the **Fig. 1(a)** , the C=O stretching frequency of Pure SG has shifted from 1627 cm^{-1} to 1612 cm^{-1}. This suggests the formation of Fe^{2+} - DTPMP complex and also Fe^{2+}- SG complex on the metal surface. DTPMP has coordinated with Fe^{2+} through N and O atoms of phosphonic acid [9]. SG has coordinated with Fe^{2+} through O atom of carbonyl group, the peak at 1421 cm^{-1} may be due to the in plane vibration of the OH group in $Zn(OH)_2$ [10] formed on the cathodic sites of the metal surface.

C. Analysis of Electrochemical Impedance spectra and Polarization Study

The Nyquist representations of the impedance behaviour of carbon steel immersed in various environments are given in Table 2. Here, for uninhibited solution the charge transfer resistance is 215 ohm cm^2, for inhibited solution containing 25 ppm DTPMP, 25 ppm SG and 10 ppm Zn^{2+} the charge transfer resistance 2740 ohm cm^2. The Charge transfer resistance and double layer capacitance derived from these curves are given Table 3. At the same time the double layer capacitance (C_{dl}) value getting decreases from 6.22 x 10^{-6}µF / cm^2 to 3.96 x 10^{-8} µF / cm^2. It is clear that the addition of inhibitor increases the value of charge transfer resistance (R_{ct}) and decreases the value of Double layer capacitance (C_{dl}). The decreases in C_{dl} attributed to increases in thickness of electronic double layer [11]. The IE obtained by the EIS is about 92.1%.

According to the Polarization study, in presence of inhibitor, the IE was about 75 %. When Carbon steel is immersed in 60 ppm Cl^- environment the corrosion current I_{corr} is 1.26 x 10 $^{-5}$ A/cm^2. When 25 ppm DTPMP, 25ppm SG, 10 ppm Zn^{2+} are added the corrosion current decreases to 3.17 x 10^{-6} A / cm^2. The significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of inhibitor. For the Blank system the corrosion potential is - 598 mV vs SCE, for the inhibitor system the potential of corrosion is -0.472 mV vs SCE. This is shown in the Table 2.This suggests this formulation controls the anodic reaction predominantly. From the Polarization curves it can be inferred that Zn $(OH)_2$ formed on the metal surface retards the oxygen reduction reaction and thus controls the cathodic reaction of the metal. The DTPMP- SG – Zn^{2+} system shifts the corrosion potential to anodic side. Thus the ternary inhibitor formulation acts as anodic inhibitors. This indicates the protective film formed on the metal surface.

TABLE 2. EIS AND POLARIZATION PARAMETERS OF CARBON STEEL IMMERSED IN 60 PPM CL^- ENVIRONMENT OBTAINED BY ELECTROCHEMICAL STUDY.

Inhibitor System: DTPMP – SG – Zn^{2+} Immersion Period: 3 Days pH = **7**

S.No	Cl^- [ppm]	DTPMP [ppm]	SG [ppm]	Zn^{2+} [ppm]	$E_{corr.}$ [mV vs SCE]	b_c [mV]	b_a [mV]	I_{corr} [A/cm^2]	R_t [Ω cm^2]	C_{dl} [µF / cm^2]	I.E % (EIS)	I.E % (Polari)
1	60	0	0	0	-598	5.27	5.18	1.26×10^{-5}	215	6.22×10^{-6}	75	92.1
2	60	25	25	10	-472	6.34	5.83	3.17×10^{-6}	2740	3.96×10^{-8}		

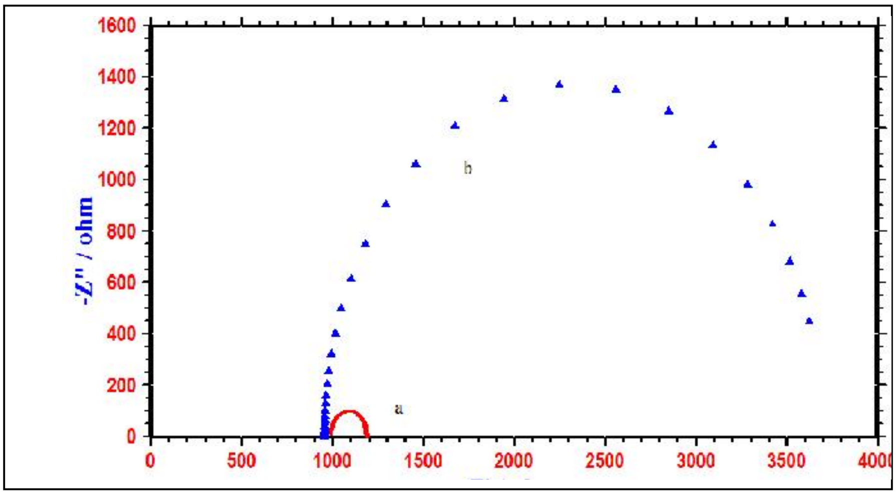


Figure.2. EIS curves of carbon steel immersed in various test solutions

a) 60 ppm Cl^- b) 60 ppm Cl^- + 25 ppm DTPMP + 25 ppm SG + 10 ppm Zn^{2+}

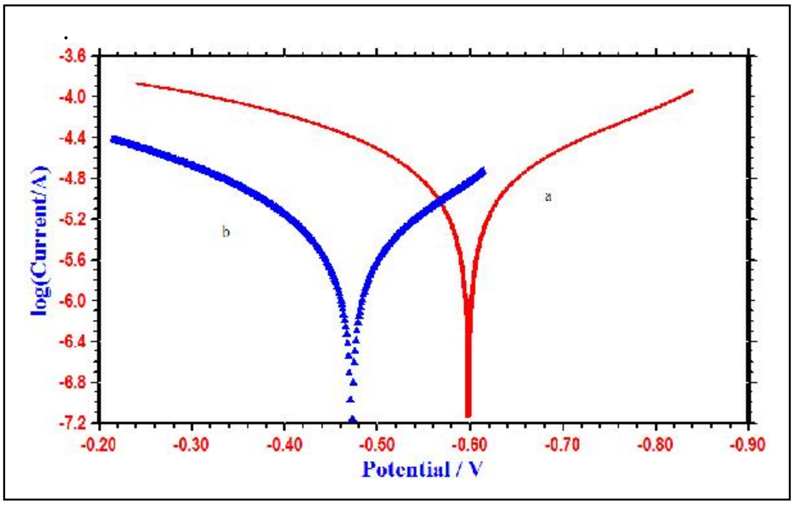
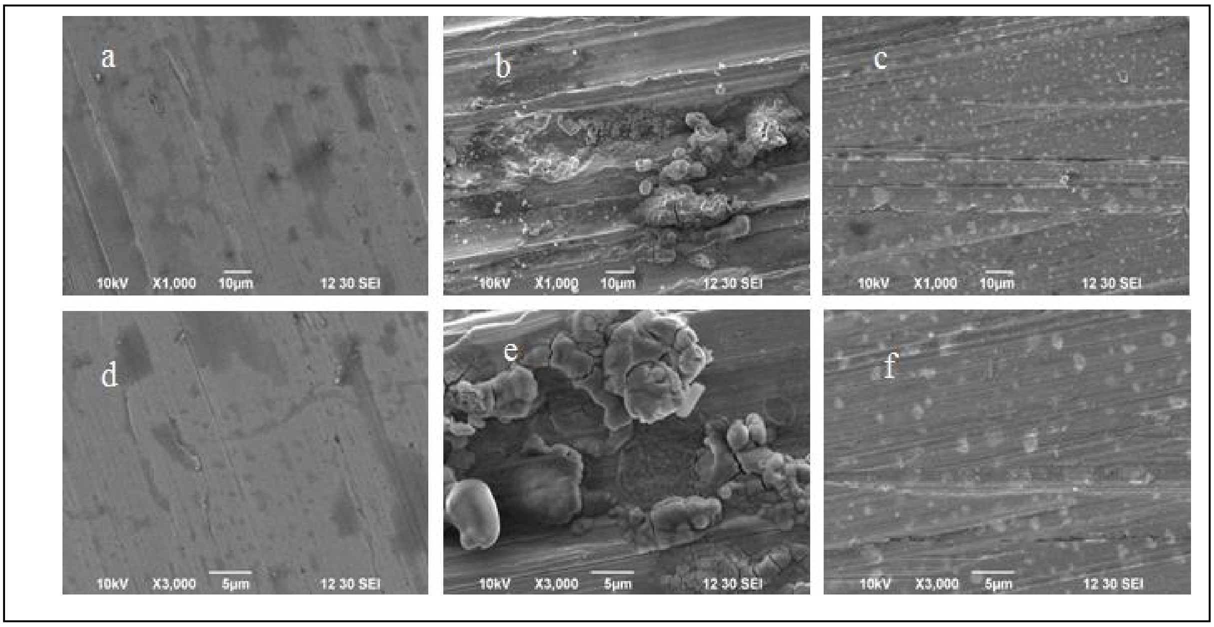


Figure.3. Polarization curves of carbon steel immersed in various test solutions

a) 60 ppm Cl^- b) 60 ppm Cl^- + 25 ppm DTPMP + 25 ppm SG + 10 ppm Zn^{2+}

D. SEM Analysis

The SEM (Scanning Electron Microscope) images taken for the system in presence and



absence of an inhibitor. Normally for comparison, control metal, Metals without inhibitors (Uninhibited), in presence of inhibitors (Inhibited), was taken with one day immersion period in 60 ppm Cl^- . The SEM micrographs of polished Carbon steel (Control metal) is shown in Fig. 4.a,d with X 1000 and x 3000 magnification respectively, from the images it was observed that the surface is smooth. This indicates the absence of any corrosion products on the metal surface. The SEM images of Carbon steel which is immersed in 60 ppm Cl^-. Here, the roughness of the metal surface increases which shown in the Fig. 4.b, e. In presence of inhibitor formulations the surface coverage increases is shown in Fig. 4.c,f , the formulations are 60 ppm Cl- + 25 ppm DTPMP + 25 ppm SG + 10 ppm Zn^{2+}. This formulation forms a protective film on the metal surface by the way of forming insoluble complexes. The surface covered by a thin layer of inhibitor which effectively controls the dissolution of Carbon steel.

IV. CONCLUSION

The Inhibition Efficiency of Carbon steel immersed in 60 ppm Cl^- in the absence and presence of inhibitor 25 ppm DTPMP, 25 ppm SG and 10 ppm Zn^{2+} has been evaluated. The influence of SG on the inhibition efficiency of DTPMP – Zn^{2+} system has also been evaluated.

According to the Weight-loss measurements the inhibitor system 25 ppm DTPMP, 25 ppm SG and 10 ppm Zn^{2+} have 96 % Inhibition Efficiency.

Potentiodynamic polarization study reveals that this inhibitor formulation functions as an anodic inhibitor.

The FT – IR spectral data indicates that the protective film consists of Fe^{2+} - DTPMP complex, Fe^{2+} - SG complex and $Zn(OH)_2$.

AC Impedance spectra and SEM micrographs reveal that the formation of protective film on the surface of Carbon Steel.

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