

Inhibition Of Corrosion Of Carbon Steel In A Well Water By Sodium Molybdate – Zn²⁺ – A Phosphonic Acid System

R.Epshiba^{1*}, A. Peter Pascal Regis¹, C. Rajarathinam¹, R. Betsy Clarebel¹ and S.Rajendran²

¹. Department of Chemistry, St. Joesph's College, Thricky, Tamil Nadu, India 624005; Emails: hphzi_r@aol.com, drpascalregis@gmail.com, rajarathnamorg@gmail.com, rclarebel@gmail.com

². Department of Chemistry, RVS School of Engineering and Technology Dindigul, Tamil Nadu, India 624005; Email: SuSRajendra@gmail.com.

Abstract: The aim of this present work is to study, the corrosion behaviour of carbon steel in well water in the presence of sodium molybdate (SM)-Zn²⁺-2-chloroethylphosphonic acid (2-CEPA) solutions. In this paper, detailed studies on 2-CEPA as second synergist in the formulation containing relatively low levels of sodium molybdate (SM)-Zn²⁺ in the corrosion inhibition of carbon steel are presented. Thus, the ternary system containing 100ppm of SM, 25ppm of Zn²⁺, and 250ppm of 2-CEPA is quite effective. Electrochemical studies and FTIR spectral studies and weight loss study have been employed. Polarization study reveals that SM-Zn²⁺-2-CEPA system functions as an anodic inhibitor, and the formulation controls the anodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe²⁺-MoO₄²⁻ Complex, Fe²⁺-2-CEPA complex at anodic site and Zn(OH)₂ complex at cathodic site. Based on the above results a mechanism of corrosion inhibition is proposed.

[R. Epshiba, A. Peter Pascal Regis, C. Rajarathinam, R. Betsy Clarebel and S. Rajendran. **Inhibition Of Corrosion Of Carbon Steel In A Well Water By Sodium Molybdate – Zn²⁺ – A Phosphonic Acid System.** *Researcher* 2015;7(3):66-73]. (ISSN: 1553-9865). <http://www.sciencepub.net/researcher>. 11

Keywords: carbon steel, corrosion inhibition, sodium molybdate, 2-chloroethylphosphonic acid, well water, synergistic effect.

1. Introduction

Mild steel has many industrial applications because of its easy availability, low cost, uncomplicated fabrication of it into water pipe lines [1,2], cooling water systems [3], boilers etc. However, they are susceptible to different forms of corrosion induced by chloride and so on. One of the most important methods in corrosion protection is to use inhibitors [4-5]. Inhibitors should be of low toxicity and easily biodegradable in order to meet environmental protection requirements. Molybdate is an environmentally friendly inhibitor and has been extensively studied for its application in the protection of iron, Zinc and Aluminium substrates in neutral, acidic and alkaline solutions. Normally it is not feasible to use molybdate alone as a corrosion inhibitor due to its low inhibition ability at low concentrations of molybdate and high cost. In most cases, the combinations of molybdate with co-inhibitors were described in the literature [6-10]. However, previous literature has not reported the use of molybdate as the corrosion inhibitor for mild steel with more than one co inhibitors. Phosphates in the form of poly phosphates control the corrosion of ferrous metals [11]. They act as cathodic inhibitors [12,13]. Phosphonic acid is used as a corrosion inhibitor for the corrosion control in industrial boiler water and municipal water treatment [3]. Saha et al [15] studied the mechanism of phosphate based

cooling system corrosion inhibitors in a mild steel plant. Their inhibition properties were increased by the addition of metallic ions [16]. Their metallic ions form insoluble complexes with phosphonic acids and repair the porous oxide and prevent for the corrosion. Predominantly Zn²⁺ ions are used for elevating the corrosion inhibiting properties of phosphonic acids [17,18]. The Zn-Phosphonate complexes showed excellent corrosion inhibition as compared to other metal cations. For this present work, the first synergist is Zn²⁺ and second synergist is 2-CEPA with sodium molybdate (SM). Rajendran et al [19] have discussed polarization study of mild steel in neutral aqueous environment containing 60ppm Cl⁻ in the presence of 2-CEPA. The present study evaluates the synergistic effect of sodium molybdate-Zn²⁺ system; estimates the influence of 2-CEPA on the IE of SM-Zn²⁺ system; a studies mechanistic aspects of corrosion inhibition by electrochemical studies and analysis protective film by FTIR spectroscopy.

2. Experimental

2.1. Preparation of the Specimen

Carbon steel specimens (0.026 % S, 0.06 % P, 0.4 % Mn, 0.1 % C, and the rest iron) of the dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight loss method and surface examination studies.

2.2. Weight-Loss Method

Carbon steel specimens in triplicate were immersed in 100 ml of the well water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for 3 days.

The weights of the specimens before and after immersion were determined using a Digital Balance Model AUY 220 SHIMADZU. The corrosion products were cleaned with Clarke's solution. It can be prepared by dissolving 20 gms of Sb_2O_3 and 50 gms of $SnCl_2$ in one litre of Conc.HCl of specific gravity (1.9)[20]. The corrosion IE was then calculated using the equation.

$$IE = 100 [1 - (W_2/W_1)] \%$$

where W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence of inhibitor. Corrosion rate was calculated using the formula

$$\text{Millimetre per year} = 87.6 W / DAT$$

$$W = \text{weight loss in milligrams}$$

$$D = \text{density of specimen } g/cm^3 = 7.87 \text{ gm/cm}^3$$

$$A = \text{area of specimen} = 10cm^2$$

$$T = \text{exposure in hours} = 72 \text{ hrs.}$$

2.3. Surface Examination Study

The carbon steel specimens were immersed in various test solutions for a period of 3 days. After 3 days, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by various surface analysis techniques.

2.4. Fourier Transform Infrared Spectra

These spectra were recorded in a Perkin-Elmer-1600 spectrophotometer using KBr pellet. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr, and making the pellet.

2.5. Potentiodynamic Polarization

Polarization studies were carried out in a CHI-electrochemical work station with impedance model 660A. It was provided with IR compensation facility. A three- electrode cell assembly was used. The working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a , and cathodic = b_c were calculated and a linear polarization study was done. The scan rate (V/S) was 0.01. Hold time at (E_{fcs}) was zero and quiet time (s) was two.

2.6. AC Impedance Spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer

resistance (R_t) and the double layer capacitance (C_{dl}) were calculated. AC impedance spectra were recorded with initial $E_{(v)} = 0$, high frequency (Hz) = 1×10^5 , low frequency (Hz) = 1, amplitude (V) = 0.005, and quiet time (s) = 2.

2.7. Synergism Parameter

The synergism parameter can be calculated by using the equation indicates the synergistic effect existing between the inhibitors [21-23]. S_1 value is found to be greater than one suggesting that the synergistic effect between the inhibitors is

$$S_1 = 1 - I_1 + 2 / 1 - I_{1+2}$$

where

I_1 = inhibition efficiency of substance 1

I_2 = inhibition efficiency of substance 2

I_{1+2} = combined inhibition efficiency of substance 1 and 2.

If synergistic effect exists between the inhibitors, S_1 value will be greater than one.

2.8. Analysis of Variance (F-Test)

An F-test was carried out to investigate whether the synergistic effect existing between inhibitor systems is statistically significant [24]. If F-value is greater than 5.32 for 1,8 degrees of freedom, the synergistic effect proves to be statistically significant. If it is less than 5.32 for 1,8 degrees of freedom, it was statistically insignificant at a 0.05 level of significance.

3. Results And Discussion

3.1 Weight-Loss Study

The physicochemical parameters of well water are given in Table 1. The corrosion inhibition efficiencies and the corresponding corrosion rates (millimetre per year) of sodium molybdate- Zn^{2+} systems are given in Table 2.

Table 1. Physico-Chemical Parameters of Well Water

Parameter	Value
pH	8.38
Conductivity	3110 μ mhos/cm
Chloride	665 ppm
Sulphate	14ppm
TDS	2013ppm
Total hardness	1100ppm

The inhibition efficiency (IE) of sodium molybdate (SM) in controlling corrosion of carbon steel immersed in well water for a period of 3 days in the absence and the presence of Zn^{2+} is given in Table 2. It can be seen from the data that SM alone shows some IE, whereas Zn^{2+} alone is found to be corrosive. When SM is combined with Zn^{2+} ions, it is found that the IE increases with the concentration of Zn^{2+} ions. For example, 250 ppm SM has only 64% IE and 50 ppm of Zn^{2+} has only 10% IE. Interestingly, their combination shows 92% IE. This suggests a

synergistic effect between the binary inhibitor formulation SM and Zn^{2+} ions; SM is able to transport Zn^{2+} towards the metal surface.

Table 2. 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

SM (ppm)	Zn^{2+} (ppm)			
	0	25	50	75
CR(mmy)				
0	0.1174	0.1115	0.1056	0.0927
50	0.0950	0.0845	0.0763	0.0481
100	0.0845	0.0704	0.0493	0.0258
150	0.0751	0.0493	0.0340	0.0187
200	0.0587	0.0352	0.0211	0.0117
250	0.0422	0.0293	0.0093	0.0058
IE(%)				
0	-	5	10	21
50	19	28	35	59
100	28	40	58	78
150	36	58	71	84
200	50	70	82	90
250	64	75	92	95

3.1.2. Evaluation of synergistic effect of 2-CEPA with molybdate- Zn^{2+} system

In order to examine the role of 2-CEPA in the ternary inhibitor formulation, experiments were conducted with 2-CEPA alone, SM, and with Zn^{2+} + 2-CEPA in a wide concentration range. The highest inhibition efficiencies with these systems are shown in Table 3. The synergistic effect in the SM- Zn^{2+} -2-CEPA system is evident from the data in Table 3. The Zn^{2+} ion acts as one synergist and 2-CEPA acts as the other. From the data in Table 3, it is seen that at relatively higher concentrations of both SM, Zn^{2+} and 2-CEPA, 71% IE was obtained. However, such an efficiency is not obtained with combinations of SM and 2-CEPA, even at relatively high concentrations. Thus, it may be concluded that Zn^{2+} is the primary synergist and 2-CEPA is the secondary synergist and both play a significant synergistic role in inhibiting corrosion. Hence, the highest IE is obtained at such low concentrations of each of the components in the ternary inhibition formulation.

Table 3. Corrosion Rates (CR) and Inhibition Efficiencies (IE) of Carbon Steel in Well Water, in the Absence and the Presence of Inhibitors and Inhibition Efficiency (IE) Obtained by Weight-Loss Method

SM ppm	Zn^{2+} ppm	2-CEPA ppm	IE %	CR mmy
0	0	0	-	0.1174
100	0	0	28	0.0950
0	25	0	5	0.1115
0	0	250	26	0.0868
100	25	0	40	0.0704
100	25	50	49	0.0598
100	25	100	56	0.0516
100	25	150	63	0.0434
100	25	200	67	0.0387
100	25	250	71	0.0340
100	0	250	42	0.0680
0	25	250	37	0.0739

3.1.1. Synergism parameter

The values of synergism parameters are shown in Table 4. The values of S_1 are greater than one, suggesting a synergistic effect. S_1 approaches 1 when no interaction exists between the inhibitor compounds. When $S_1 > 1$, this points to the synergistic effect. In the case of $S_1 < 1$, the negative interaction of inhibitors prevails (i.e., corrosion rate increases).

Table 4. Synergism Parameter of Carbon Steel Immersed in Well Water in the Presence and Absence of Inhibitor

SM+ Zn^{2+} (I_2) IE (%)	2-CEPA (I_1) IE (%)	SM- Zn^{2+} -2-CEPA (I'_{1+2}) IE (%)	S_1
40	12	49	1.03
40	16	56	1.14
40	20	63	1.29
40	23	67	1.40
40	26	71	1.64

3.1.2. Analysis of variance (ANOVA)

F-test is used if the synergistic effect exists between inhibitors is statistically significant [24]. The results are given in Table 5. Influence of various concentrations of 2-CEPA (50, 100, 150, 200, and 250 ppm) on the inhibition efficiencies of SM(100ppm) - Zn^{2+} (25 ppm) is tested in Table 4. The calculated F-value is 8.354. It is statistically significant, since it is greater than the critical F-value (5.32) for 1, 8 degrees of freedom of 0.05 level of significance. Hence, it is concluded that the inhibition efficiencies of the SM- Zn^{2+} -2-CEPA system is statistically significant.

Table 5. Distribution of F Value between the Inhibition Efficiencies of SM-Zn²⁺ and SM-Zn²⁺-2-CEPA Systems

Source of variance	Sum of squares	Degrees of freedom	Mean square	F	Level of significance of F
Between	2118.4	1	2118.4	8.354	P>0.05
Within	2028.4	8	253.55		

3.2. Analysis of FTIR Spectra

FTIR spectra have been used to analyze the protective film formed on metal surface [25,26]. FTIR spectrum of pure sodium molybdate is given in Figure 1a. The Mo-O stretching frequency appears at 824 cm⁻¹. The FTIR spectrum of pure 2-CEPA is shown in Figure 1b. The P-O stretching frequency appeared at 1006 cm⁻¹. The FTIR spectrum of the film formed on the metal surface after immersion in the well water for 3 days containing 100ppm of sodium molybdate , 25ppm of

Zn²⁺ and 250ppm 2-CEPA is shown in Figure 1c. The P-O stretching frequency shifted from 1006 cm⁻¹ to 1081 cm⁻¹. This suggests that the oxygen atoms of 2-CEPA are coordinated with Fe²⁺ on the anodic sites of the metal surface, resulting in the formation of Fe²⁺-2-CEPA complex [27,28]. The Zn-O stretching frequency appears at 669 cm⁻¹ and the stretching frequency due to -OH appears at 3428 cm⁻¹. Therefore, it is concluded that Zn(OH)₂ is formed on cathodic sites of the metal surface [29].

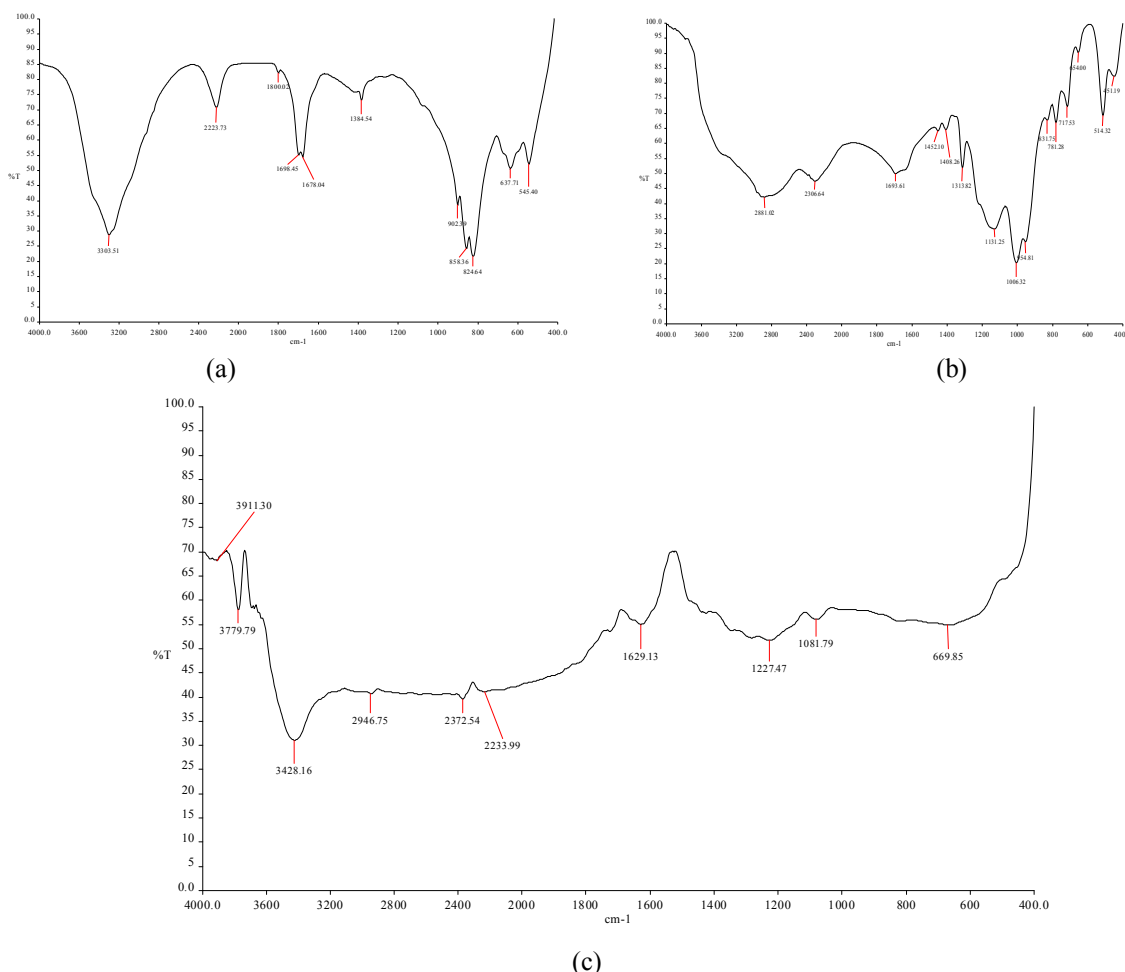


Figure 1. FTIR Spectrum

(a) Pure sodium molybdate (b) Pure 2-CEPA

(c) Film formed on metal surface after the immersion in well water containing 100ppm SM - 25ppm of Zn²⁺ and 250ppm 2-CEPA

3.3. Analysis of Potentiodynamic Polarization Curves

A polarization study has been used to detect the formation of protective film on the metal surface [30,31]. The potentiodynamic polarization curves of carbon steel immersed in well water medium are shown in Figure 2. The corrosion parameters of carbon steel immersed in various test solutions obtained by polarization study are given in Table 6.

When mild steel is immersed in well water, the corrosion potential is -763 mV vs SCE. The formulation consisting of 100ppm SM + 25ppm Zn^{2+} and 250ppm 2-CEPA shifts the corrosion potential to -601 mV vs SCE. This suggests that the anodic reaction is controlled predominantly, since more molybdate ions are transported to the anodic sites in the presence of Zn^{2+} .

Table 6. Corrosion Parameters of Carbon Steel in Well Water in the Presence of Inhibitors, Obtained by Polarization Study

System	E_{corr} mV vs SCE	b_a mV	b_c mV	LPR Ω cm ²	I_{corr} A/cm ²
Well water (WW)	-763	148	64	496.9	3.92×10^{-5}
WW + SM (100ppm) + Zn^{2+} (25ppm) + 2-CEPA (250ppm)	-601	155	67	910.6	2.226×10^{-5}

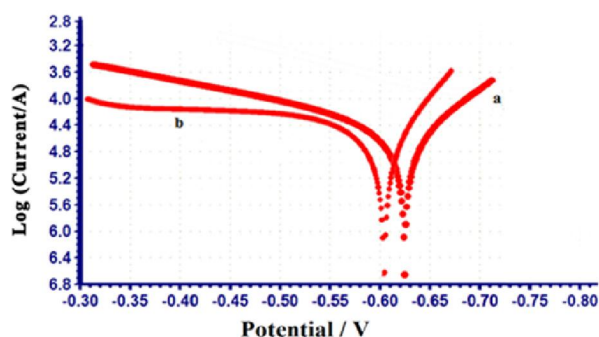


Figure 2. Polarization curves of carbon steel immersed in various test solutions

a) Well water b) Well water containing 100ppm of sodium molybdate, 25ppm of Zn^{2+} and 250ppm of 2-CEPA

The corrosion current I_{corr} for well water is 3.92×10^{-5} A/cm². When SM (100 ppm) Zn^{2+} (25ppm) and (250ppm) 2-CEPA are added, it decreases to 2.226×10^{-5} A/cm². The significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of the inhibitor. Both the anodic and cathodic Tafel slopes are shifted in the presence of the inhibitor. However, a shift of 7 mV in the anodic Tafel slope (b_a) is much higher as compared to a shift of 3 mV in the cathodic Tafel slope for the blank and SM (100ppm)- Zn^{2+} (25 ppm)-2-CEPA(250ppm) formulations. Thus, it can be concluded that this inhibitor formulation acts as an anodic inhibitor. This indicates that a protective film is formed on the metal

surface. This study clearly reveals the fact that the addition of increasing concentrations of SM- Zn^{2+} -2-CEPA moves the corrosion potential towards less value and reduces the corrosion rate. In the presence of these combinations, I_{corr} value decreases.

3.4. Analysis of AC Impedance Spectra

AC impedance spectra have been used to detect the formation of film on the metal surface. If a protective film is formed, the charge transfer resistance increases and double layer capacitance value decreases [32,33]. The AC impedance spectra of carbon steel immersed in various solutions are shown in Figure 3. The AC impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}), are given in Table 7. When carbon steel is immersed in well water, the R_t value is 79.71Ω cm² and the C_{dl} value is 5.21×10^{-8} μ F/0.5 cm². When MoO_4^{2-} , Zn^{2+} and 2-CEPA are added to well water, the R_t value increases tremendously from 79.71Ω cm² to 163.56Ω cm² and the C_{dl} decreases from 5.21×10^{-8} μ F/0.5 cm² to 2.537×10^{-8} . This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of MoO_4^{2-} - Zn^{2+} -2-CEPA system. The impedance value increases from 2.007 to 2.367. This accounts for the high inhibition efficiency of SM- Zn^{2+} and 2-CEPA system and a protective film is formed on the mild steel surface. This is also supported by the fact that for the inhibitor system the phase angle increases from 29.33° to 29.52° .

Table 7. Impedance parameter of carbon steel in well water in the absence and presence of inhibitors, obtained by AC Impedance method

System	R_p , ohm cm ²	C_{dl} , F cm ⁻²	Impedance, log(Z ohm ⁻¹)	Phase angle
Well water (WW)	79.71	5.21×10^{-8}	2.007	29.33°
WW + SM + Zn ²⁺ + 2-CEPA	163.56	2.537×10^{-8}	2.367	29.52°

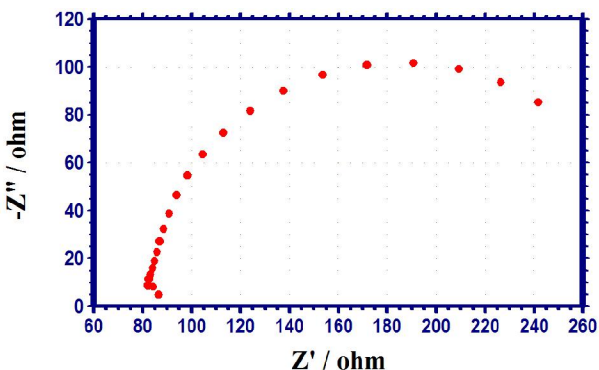
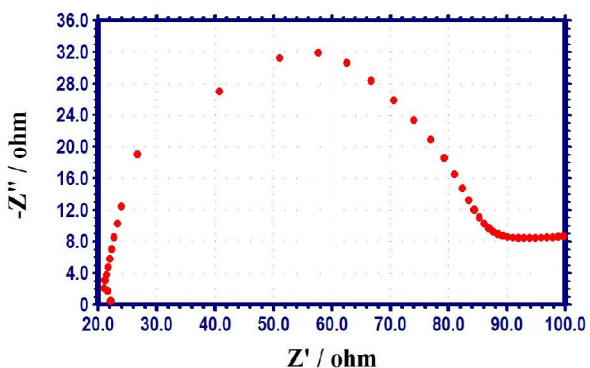


Figure 3. Nyquist plots of carbon steel immersed in various test solution

a) Well water b) Well water + SM 100ppm + Zn²⁺ 25ppm + 2-CEPA 250ppm

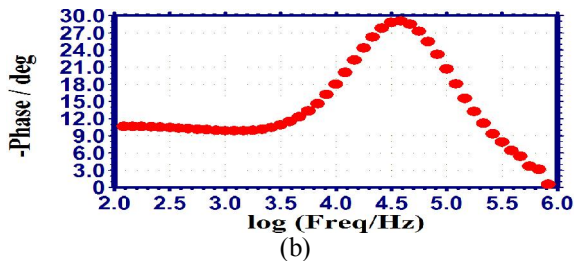
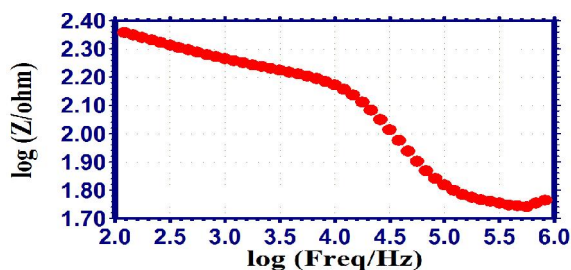
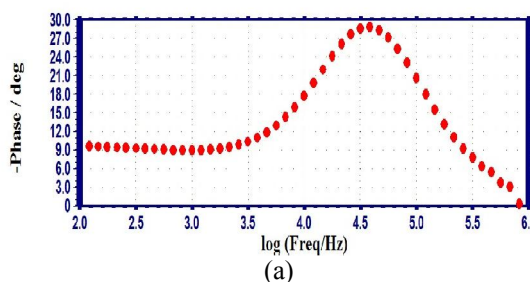
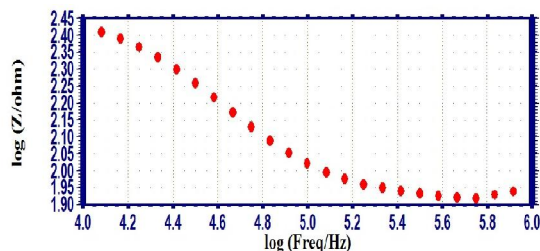


Figure 4. Bode plots of carbon steel immersed in various test solution

a) Well water b) Well water + SM 100ppm + Zn²⁺ 25ppm + 2-CEPA 250ppm

3.5. Mechanism of Corrosion Inhibition

In order to explain the experimental results, the following mechanism of corrosion inhibition is proposed. The mechanistic aspect of the inhibition of carbon steel in well water by SM-Zn²⁺ and 2-CEPA can be explained in terms of complexation and adsorption.

i. Before immersion of carbon steel in well water environment, SM, Zn²⁺ and 2-CEPA- Zn²⁺ form complexes, viz., Zn²⁺-SM, Zn²⁺-2-CEPA, and Zn²⁺-SM-2-CEPA. These complexes are in equilibrium in the solution with free Zn²⁺, SM, and 2-CEPA ions.

ii. During the dissolution of iron, the pH increases at the metal/electrolyte interface due to oxygen reduction. Thus, Zn(OH)₂ precipitate may take place at cathodic sites [34,35], thus decreasing the rate of further oxygen reduction.

iii. Addition of phosphonic acids (PA) reduces metal dissolution; this may be due to adsorption and complex formation at the surface [36–39] with the combined application of Zn²⁺ and 2-CEPA. The corresponding anodic and cathodic reactions of the metal can be generalized as follows. Zn²⁺ inhibits the local cathodic region and the local anodic region was inhibited by 2-CEPA.

iv. The Zn-PA complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe- PA complex, which is more stable than Zn-PA [35]. The released Zn²⁺ causes Zn(OH)₂ precipitation at the local cathodic sites. Thus, the protective film consists of an Fe-PA complex and Zn(OH)₂.

v. The film formed on the metal surface of the carbon steel consists of oxides/hydroxides of iron and zinc. It is also likely to comprise complexes of Fe²⁺ and Zn²⁺ with SM as well as with 2-CEPA.

vi. The FTIR spectra of the surface film suggests the formation of these complexes and the presence of Zn(OH)₂ in the surface.

4. Conclusions

A formulation consisting of Zn²⁺, sodium molybdate, and 2-chloroethylphosphonic acid can be used as a potent inhibitor to prevent the corrosion of carbon steel in well water. 2-CEPA plays an excellent synergistic role in the SM-Zn²⁺-2-CEPA system. The ternary system SM (100ppm)-Zn²⁺(25ppm)- 2-CEPA (250ppm) is effective and has 71% IE. Significant synergism was attained by the combined application of SM-Zn²⁺-2-CEPA. The concentrations of both SM and Zn²⁺ are reduced, and 2-CEPA, which is environmentally friendly, is required only at low concentrations. Thus, this new inhibitor formulation is more environment-friendly. The inhibitor formulation acts as an anodic inhibitor. Both SM and 2-CEPA form stable complexes with metal ions in the metal

surface. The protective film consists of Zn(OH)₂ and complexes of Fe²⁺ and Zn²⁺ with 2-CEPA and SM.

Acknowledgment

Though only my name appears on the cover, a great peoples have contribute to this production. I owe my credit to all those people who have made this subject possible and because of whom my graduate experience has been one that I will cherish forever. The authors are thankful to their respective managements for their help and encouragement and to the University Grants Commission for financial assistance.

References

1. R.E.Melchers, R.Jeffery, *Corrosion Reviews*, 1(2005) 84.
2. R.E.Melchers,R.Jeffery, *Corrosion Reviews*, 6(2005) 297
3. G.Saha, N.Kurmai, N.Hakerman, *Journal of Physis.Chem*, 59 (1955) 707.
4. Q-J.Xu, Z.Lu,G.D.Zhou, *Journal of East China University of Science and Technology*, 2(29)(2003) 493.
5. Q-J.Xu, Z.Lu, G.D.Zhou, *Acta ChemicaSinica*, 59 (2001) 950.
6. Z.Baiqing, L.Xia, X.Shujiao, *Materials Performance*, 47 (9) (2008) 50.
7. M.A.Amin, H.H.Hassan, O.A.Hazzazi, M.M.Qhatani, *Journal of Applied Electrochemistry*, (2008)1.
8. M.Abdallah, A.Y.El-Etre, M.G.Soliman, E.M.Mabrouk, *Anti-Corrosion Methods and Materials*, 53 (2)(2006) 118.
9. S.M.A.Shibli, V.S.Saji, *Corrosion Prevention and Control*, 50(3) (2003) 136.
10. J.M.Abd El Kader, A.A.El Warraky, A.M. Abd El Aziz, *British Corrosion Journal* 33 (2) (1998) 152.
11. K.Madhavan, S.Muralidharan, S.K.V.Iyer, *Bull. Electrochem* 17 (2001) 215.
12. G.B.Hatch, *Ind. Engg. Chem* 44 (1952) 1775.
13. K.S.Rajagopalan and K.Venu, *Ind.J.Technol* 6 (1968) 239.
14. H.S.Awad, *Corr.Engg. Sci and Technol* 240 (2005)57.
15. E.A.Ashour, H.S.Hegazy and V.G.Ateya, *Adsorp Sci and Technol*, 20 (2002) 485.
16. H.S.Awad and S. Turgoose, *British Corrosion Journal*, 37 (2003) 147.
17. E.Kalman, B. Varhegyi, I.Bako, I.Felhosi, Fr.I. Kalma and A. Shaban, *J.Electrochem, Soc*, 141 (1994) 3357.
18. A.Veres, G.Rainhard and E.Kalman, *British Corrosion Journal*, 27 (1992) 147.

19. S. Rajendra, B.V. Apparao and N.Palaniswamy, "Mechanism of corrosion inhibition by the 2-chloroethyl phosphonic acid - Zn²⁺ system", *Anti-Corrosion Methods and Materials*, 47(3), 147-151.
20. G. Wranglen, "Synergistic Effect of 2-Chloroethyl Phosphonic Acid and Zn²⁺", *Introduction to Corrosion and Protection of Metals*. London: Chapman & Hall, (1985) 236.
21. C.W.Cui, S.F.Li, H.Yang, W.T.Feng, Y. Liu, Y.J. Jiao, *Cailiao Kexue yu Gongyi/Material Science and Technology* 14 (6) (2006) 608.
22. S.Rajendran, A.J.Amalraj, J.W.Sahayaraj, R.J.Rathish, N.Anthony, N.Palaniswamy, *Transactions of the SAEEST (Society for Advancement of Electrochemical Science and Technology)*, 40 (1) (2005) 35.
23. G.Waranglen, *Introduction to Corrosion and Protection of Metals* [Chapman and Hall, London] (1986) 236.
24. K.Aramaki and N.Hacherman, *J.Electrochem*, 22 (7) (2006) 311.
25. G. Ruba Helen Florence, A. Noreen Anthony, J. Wilson Sahayaraj, A. John Amalraj, and Susai Rajendran, "Corrosion Inhibition of Carbon Steel by Adipic Acid-Zn²⁺ System", *Indian Journal of Chemical Technology*, 12 (2005) 472-476.
26. S. Rajendran, S. P. Sridevi, N. Anthony, A. John Amalraj, and M. Sundaravadivelu, "Corrosion Behavior of Carbon Steel in Polyvinyl Alcohol", *Anti-Corrosion Methods and Materials*, 52 (2005) 102-107.
27. A. D. Cross, *Introduction to Practical Infrared Spectroscopy*. London: Butterworth Scientific Publication, 1960, p. 73.
28. K. Nakamoto, *Infrared & Raman Spectra of Inorganic & Coordination Compounds*. New York: Wiley Interscience, 1986, p. 166.
29. R.M.Silverstein, F.X.Webster : *Spectrometric Identification of Organic Compounds*, VI Edition, *Wiley Student Edition*, 2007 p-108
30. S. Rajendran, B. V. Apparao, N. Palaniswamy, A. J. Amalraj, and M. Sundaravadivelu, "The Role of Phosphonates as Transporters of Zn²⁺ Ions in the Inhibition of Carbon Steel in Neutral Solutions Containing Chlorides", *Anti-Corrosion Methods and Materials*, 49 (2002) 205.
31. S. Rajendran, B. V. Apparao, and N. Palaniswamy, "Corrosion Inhibition by Phosphonic Acid -Zn²⁺ Systems for Mild Steel in Chloride Medium", *Anti-Corrosion Methods and Materials*, 47 (2000) 359.
32. J. Sathiabama, Susai Rajendran, and J. Arockia Selvi, "Eriochrome Black T as Corrosion Inhibitor for Carbon Steel in Well Water", *Bulletin of Electrochemistry*, 22 (2006) 363.
33. Susai Rajendran, M. Manivannan, J. Wilson Sahayaraj, J. Arockia Selvi, J. Sathiabama, A. John Amalraj, and N. Palaniswamy, "Corrosion Behavior of Aluminium in Methyl Orange Solution at pH 11", *Trans. SAEEST*, 41 (2006) 63.
34. D. Gopi, N. Bhuvaneshwaran, and S. Rajeswari, "Synergistic Effect of Zn²⁺, 3-Phosphonopropionic Acid and Non-Ionic Surfactant (triton X-100) on the Corrosion Inhibition of 304 Stainless Steel in Ground Water Media", *Bulletin of Electrochem*, 18(2002), pp. 29-34.
35. D. Gopi and S. Rajeswari, in *Proceedings of International Conference on Advances in Surface Science and*
36. D. Gopi and S. Rajeswari, in *Proceedings of International Conference on Advances in Surface Science and Engineering*, (INSURE), Chennai, India, 21-23 Feb, 2001, p. 210
37. D. Gopi and S. Rajeswari, in *Proceedings of NACE International Conf, Corrosion its Mitigation and Preventive Maintenance, Mumbai, India*, 1: 20-23 Nov 2000, p. 435.
38. D. Gopi and S. Rajeswari, in *Proceedings of Tenth National Congress on Corrosion Control, Conf, Madurai, India*, 6-8 Sep, 2000, p. 353.
39. Veres, G. Reinhard, and E. Kalman, "Chemical Passivation of Ferrous Materials in Presence of Salts of Phosphonic Acids", *Br Corros J.*, 27(1992), pp. 147-150. E. Kalman, "Corrosion Inhibitors", Published for EFC No. 11, Institute of Materials London, 1999.