

The effect of Zn^{2+} ion in promoting inhibitive property of phenolphthalein

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Received 2 June 2009; Revised 25 January 2010; Accepted 23 February 2010

Abstract

The inhibition efficiency of phenolphthalein in controlling corrosion of carbon steel immersed in well water has been evaluated by mass loss method both in absence and presence of zinc ion. A synergistic effect exists between phenolphthalein (PN) and Zn^{2+} . The inhibition efficiency (IE) of the PN – Zn^{2+} system decreases with increase in immersion period. Addition of N-Cetyl-N, N, N-Trimethylammonium bromide (CTAB) sodium dodecyl sulphate (SDS), sodium sulphite (Na_2SO_3) does not change the excellent inhibition efficiency of the PN- Zn^{2+} system. Polarization study suggests that the Pn- Zn^{2+} system functions as a mixed inhibitor system. AC impedance spectra reveal the presence of a protective film on the metal surface. FTIR spectra indicate that the protective film consists of Fe^{2+} -PN complex and $Zn(OH)_2$.

Keywords: Carbon steel, corrosion inhibition, phenolphthalein, dyes and synergistic effect.

1. Introduction

Several compounds such as nitrite [1, 2] phosphates [3, 4], silicates [5], sodium salicylate [6], sodium cinnamate [7], molybdate [8, 9], phosphonic acids [10, 12], polyacrylamide [13] and caffeine [14, 15] have been used as corrosion inhibitors. Talati and Gandhi have studied the effect of some dyes as corrosion inhibitors for B26S aluminium in hydrochloric acid [16, 18]. The inhibition efficiency (IE) of triphenylmethane dyes such as victoria blue, fast green, light green, malachite green, fuchsine base, fuchsine acid, crystal violet and methyl violet 6B in controlling corrosion of aluminium in phosphonic acid has been studied by Talati and Daraji using mass loss and polarization studies [19]. Though several dyes have been used as corrosion inhibitors, the mechanistic aspects of corrosion inhibition have not been studied in detail. This prompted us to investigate (i) the inhibition efficiency of phenolphthalein in controlling the corrosion of carbon steel immersed in well water in the absence and presence of zinc ion, (ii) the influence of pH and immersion period, (iii) to analyze the protective film formed on the metal surface by FTIR spectroscopy, (iv) to propose a suitable mechanism of corrosion inhibition based on the results of electrochemical studies such as polarization and AC impedance and FTIR spectra.

2. Experimental methods

2.1 Preparation of the specimens

Carbon steel specimens (0.026%S, 0.067P, 0.4%Mn, 0.17 (and the rest iron) of the dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to mirror finish and degreased with trichloroethylene and used for mass loss method and surface examination studies.

2.2 Mass loss method

Relevant data on the well water used in this study are given in Table 1.

Table 1. Parameters of well water

Parameter	Value
pH	8.38
Conductivity	3110 μ mhos/cm
Total Dissolved Solids	2013 mg/L
Chloride	665 mg/L
Sulphate	14 mg/L
Total hardness	1100 mg/L

Carbon steel specimens, in triplicate were immersed in 100 ml of well water and various concentrations of phenolphthalein in the presence and absence of Zn^{2+} (as $ZnSO_4 \cdot 7H_2O$) for a period of one day. The corrosion products were cleaned with Clarke's solution [20]. The weight of the specimens before and after immersion

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was determined using after Shimadzu balance AY62. The corrosion inhibition efficiency was calculated with equation (1)

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

where W_1 is the corrosion rate in the absence of the inhibitor and W_2 is the corrosion rate in the presence of inhibitor.

2.3 Surface examination study

FTIR spectra

The carbon steel specimens were immersed in various test solutions for one day. The specimens were taken out from the test solutions and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr so as to make it uniform through out. The FTIR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer.

2.4 Potentiodynamic polarization study

Polarization study was carried out in H and CH electrochemical impedance analyzer model CHI 660A using a three electrode cell assembly. Carbon steel was used as working electrode with platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic slope b_a and cathodic slope b_c) were calculated..

2.5 AC impedance spectra

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

3. Results and discussion

3.1 Analysis of results of mass loss study

The calculated inhibition efficiencies (IE) of phenolphthalein in controlling the corrosion of carbon steel immersed in well water

Table 2. Corrosion Rates (CR) of carbon steel in well water in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method

Inhibitor System: Phenolphthalein (PN) + Zn^{2+} Immersion Period: One day

PN mg/L	Zn^{2+} mg/L	CR mdd	IE %
0	0	59.09	-
20	0	50.23	15
60	0	47.86	19
100	0	41.95	29
140	0	40.77	31
180	0	34.86	41

both in the absence and presence of zinc ion have been tabulated in Table 2-5. The calculated values indicate the ability of phenolphthalein to be a good corrosion inhibitor. The inhibition efficiency is found to be enhanced in the presence of zinc ion.

Table 3. Corrosion Rates (CR) of carbon steel in well water in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method

Inhibitor System: Phenolphthalein (PN) + Zn^{2+} Immersion Period: One day

PN mg/L	Zn^{2+} mg/L	CR mdd	IE %
0	0	59.09	-
20	10	47.86	19
60	10	40.18	32
100	10	34.86	41
140	10	33.68	43
180	10	31.32	47

Table 4. Corrosion Rates (CR) of carbon steel in well water in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method

Inhibitor System: Phenolphthalein + Zn^{2+} Immersion Period: One day

PN mg/L	Zn^{2+} mg/L	CR mdd	IE %
0	0	59.09	-
20	25	6.50	89
60	25	5.91	90
100	25	4.73	92
140	25	3.55	94
180	25	2.36	96

Table 5. Corrosion Rates (CR) of carbon steel in well water in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method

Inhibitor System: Phenolphthalein + Zn^{2+} Immersion Period: One day

PN mg/L	Zn^{2+} mg/L	CR mdd	IE %
0	0	59.09	-
20	50	7.09	88
60	50	1.18	98
100	50	1.174	98
140	50	1.168	98
180	50	1.159	98

3.2 Influence of immersion period on inhibition efficiency

The IE of PN (60 mg/L) – Zn^{2+} (50 mg/L) (Table 6) system is found to decrease as the immersion period increases. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as Cl^- ion (665 mg/L) present in well water. There is a competition between the formations of $FeCl_2$ (and also $FeCl_3$) and Fe-PN complex on the anodic sites of the metal surface. Perusal of the results suggests that the formation of $FeCl_2$ is favoured when compared with the formation of Fe-PN complex [21,22].

Table 6. Influence of immersion period on the inhibition efficiency of the Phenolphthalein (60 mg/L) – Zn²⁺ (50 mg/L)

Inhibitor System: PN (100 mg/L) + Zn²⁺ (50 mg/L)

Immersion period (day)	1	3	5	7
System: well water CR (mdd)	59.09	21.52	14.9	17.0
System: well water + PN (60 mg/L) + Zn ²⁺ (50 mg/L) CR	1.18	1.72	1.49	2.04
IE%	98	92	90	88

3.3 Influence of N-cetyl N,N,N-trimethyl ammonium bromide (CTAB) on the inhibition efficiency of PN(60 mg/L) + Zn²⁺ 50 mg/L system

The influence of CTAB on the inhibition efficiency of PN (60 mg/L) – Zn²⁺ system is given in Table 7. It is interesting to find that the IE of the PN-Zn²⁺ system is not changed by the addition of CTAB. CTAB is a biocide. It can control the corrosion caused by bacteria. The present study reveals that the formulation consisting of PN, Zn²⁺ and CTAB has excellent corrosion inhibition efficiency. It is expected that this formulation will have excellent biocidal efficiency also. Hence this formulation may be used in cooling water system.

Table 7. Influence of N-Cetyl-N,N,N-trimethyl ammonium bromide (CTAB) on the inhibition efficiency of PN + Zn²⁺ system

Inhibitor System: PN (60 mg/L) + Zn²⁺ (50 mg/L) + CTAB
Immersion Period: One day

PN mg/L	Zn ²⁺ mg/L	CTAB mg/L	CR mdd	IE %
0	0	0	59.09	-
60	50	50	1.8	98
60	50	100	1.174	98
60	50	150	1.17	98
60	50	200	1.168	98
60	50	250	1.59	98

3.4 Influence of sodium dodecyl sulphate (SDS) on the inhibition efficiency of PN (60 mg/L) – Zn²⁺ (50 mg/L) system

The influence of SDS on the inhibition efficiency of PN (60 mg/L) – Zn²⁺ (50 mg/L) system is given in Table 8. The IE of PN – Zn²⁺ system is not changed by the addition of SDS. It can control the corrosion caused by bacteria. The present study reveals that the formulation consisting of PN, Zn²⁺ and SDS has excellent corrosion inhibition efficiency. It is expected that this formulation will have excellent biocidal efficiency also.

Table 8. Influence of Sodium dodecyl sulphate (SDS) on inhibition efficiency of PN + Zn²⁺ system

Inhibitor System: PN (60 mg/L) + Zn²⁺ (50 mg/L) + SDS
Immersion Period: One day

PN mg/L	Zn ²⁺ mg/L	SDS mg/L	CR mdd	IE %
0	0	0	59.09	-
60	50	50	1.18	98
60	50	100	1.174	98
60	50	150	1.17	98
60	50	200	1.168	98
60	50	250	1.59	98

3.5 Influence of sodium sulphite (Na₂SO₃) on the inhibition efficiency of PN (60 mg/L) – Zn²⁺ (50 mg/L) system

The influence of Na₂SO₃ on the inhibition efficiency of PN – Zn²⁺ system is given in Table 9. Addition of Na₂SO₃ has no influence on the inhibition efficiency of PN (60 mg/L) + Zn²⁺ (50 mg/L) system.

Table 9. Influence of Na₂SO₃ on the inhibition efficiency of PN + Zn²⁺ system

Inhibitor System: PN (60 mg/L) + Zn²⁺ (50 mg/L) + Na₂SO₃

PN mg/L	Zn ²⁺ mg/L	Na ₂ SO ₃ mg/L	CR mdd	IE %
0	0	0	59.09	-
60	50	50	1.8	98
60	50	100	1.74	98
60	50	150	1.7	98
60	50	200	1.68	98
60	50	250	1.59	98

3.6 Influence of pH on inhibition efficiency

The IE of the PN-Zn²⁺ has been studied at different pH of the solutions and it is calculated. IE values have been tabulated in Table 10. At pH 6 the IE is found to be 60%. This decrease in IE is due to the fact that the protective film formed on the metal surface is broken by the attack of H⁺ ions. At pH 8 the IE is 98%. Further increase in pH of the solution IE substantially. Experimental results suggest that the amount of Zn²⁺ available to transport PN towards the metal surface decreases at high pH. This may be due to the fact that zinc ions in the bulk of the solution might have been precipitated as zinc hydroxide.

Table 10. Influence of various pH on the inhibition efficiency of PN + Zn²⁺ system

Inhibitor System: PN (60 mg/L) + Zn²⁺ (50 mg/L)
Immersion Period: One day

pH	6	8	11
System : Well Water CR (mdd)	17.27	59.09	3.64
System : Well water + PN (60 mg/L) + Zn ²⁺ (50 mg/L)	6.9	1.18	0.98
CR (mdd) IE%	60	98	73

3.7 Analysis of polarization curves

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are

shown in Fig. 1a, 1b, and 1c. The corrosion parameters are given in Table 11. When carbon steel is immersed in well water the corrosion potential is -550 mV vs SCE (saturated calomel electrode). The corrosion current is $5.2480 \times 10^{-4} \text{ A/cm}^2$. When PN (60 mg/L) and Zn^{2+} (50 mg/L) are added to the above system the corrosion potential remains the same -550 mV vs SCE. This suggests that the PN- Zn^{2+} system functions as a mixed inhibitor. In the presence of this inhibitor system the corrosion current decreases from $5.2480 \times 10^{-4} \text{ A/cm}^2$ to $3.16 \times 10^{-5} \text{ A/cm}^2$. This suggests the inhibitive nature of this inhibitor system.

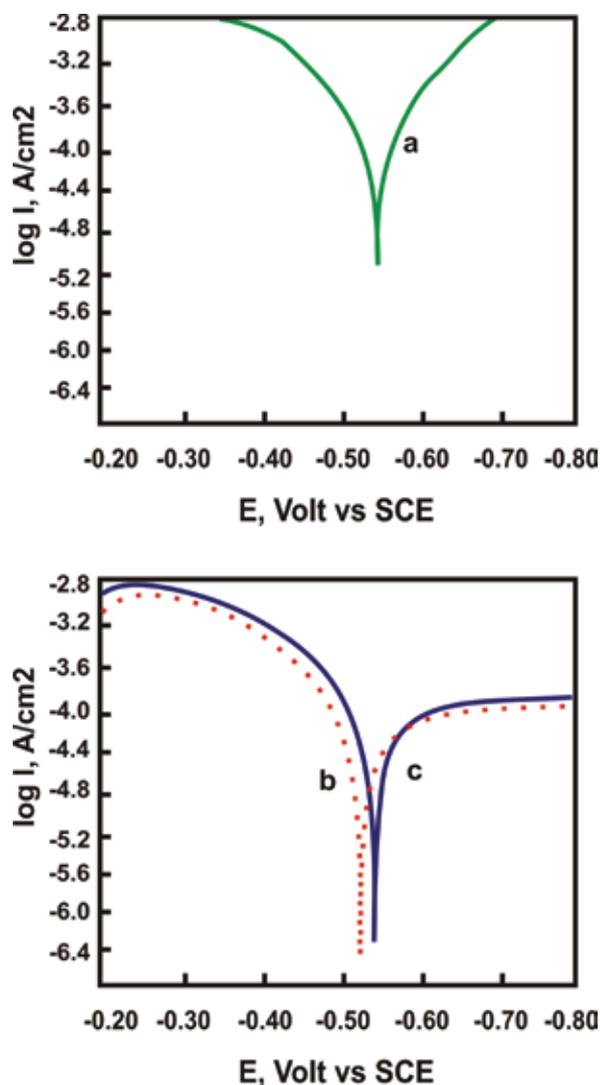


Figure 1. Polarization curves of carbon steel immersed in test solution
 (a) well water
 (b) well water + PN (60 mg/L)
 (c) well water + PN (60 mg/L) + Zn^{2+} (50 mg/L)

Table 11. Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitors
 Inhibitor: PN (60 mg/L) + Zn^{2+} (50 mg/L)

PN mg/L	Zn^{2+} mg/L	E_{corr} mV vs SCE	b_a mV/decade	b_c mV/decade	I_{corr} A/cm^2
0	0	-550	115	125	5.2480×10^{-4}
60	0	-536	96	132	5.0118×10^{-5}
60	50	-550	54	96	3.16×10^{-5}

3.8 Analysis of AC impedance spectra

The AC impedance spectra of carbon steel under our study are shown in Fig.2a, 2b and 2c. The impedance parameters have been tabulated in Table 12. When carbon steel is immersed in well water the charge transfer resistance R_t is 59.6 ohm cm^2 . The double layer capacitance C_{dl} is $4.8854 \times 10^{-8} \text{ F/cm}^2$. When the formulation consisting of PN and Zn^{2+} is added the R_t value increases to 66.52 ohm cm^2 and the C_{dl} value decreases to $4.3771 \times 10^{-8} \text{ F/cm}^2$. This increase in charge transfer resistance value (R_t) and the decrease in the double layer capacitance value (C_{dl}) confirms the formation of a protective film on the surface of the metal. This accounts for the better inhibition efficiency of the PN - Zn^{2+} system.

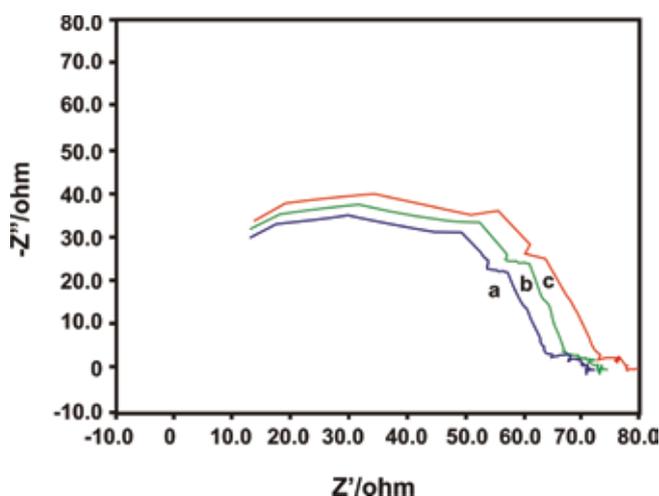


Figure 2. AC impedance spectra of carbon steel immersed in test solution
 (a) well water
 (b) well water + PN (60 mg/L)
 (c) well water + PN (60 mg/L) + Zn^{2+} (50 mg/L)

Table 12. AC Impedance parameters of carbon steel immersed in well water in the absence and presence of inhibitors
 Inhibitors: PN (60 mg/L) + Zn^{2+} (50 mg/L)

PN mg/L	Zn^{2+} mg/L	R_t ohm cm^2	C_{dl} F/cm^2
0	0	59.6	4.8854×10^{-8}
60	0	61.79	4.7121×10^{-8}
60	50	66.52	4.3771×10^{-8}

3.9 Analysis of FTIR spectra

The FTIR spectra (KBr) of pure phenolphthalein is shown in Fig.3a. The FTIR spectrum (KBr) of the film formed on the surface of the carbon steel after immersion in solution containing 60 mg/L of PN and 50 mg/L of Zn^{2+} is shown in Fig.3b. The OH stretching frequency shifts from 3319 cm^{-1} to 3435 cm^{-1} . The C=C stretching frequency shifts from 1604 cm^{-1} to 1645 cm^{-1} . In Fig.3a the C=O stretching frequency has disappeared. It was inferred that phenolphthalein has co-ordinated with Fe^{2+} through oxygen atom of OH group, carbonyl oxygen and aromatic π electron resulting in the formation of Fe^{2+} - PN complex on the anodic sites of the metal sur-

face. The band at 3435 cm^{-1} is due to -OH stretching. The band at 1350 cm^{-1} is due to Zn-O stretching. This indicates the presence of Zn(OH)_2 formed on the cathodic sites of the metal surface [22-24]. Thus FTIR spectral study lead to the conclusion that the protective film consists of Fe^{2+} - PN complex and Zn(OH)_2 .

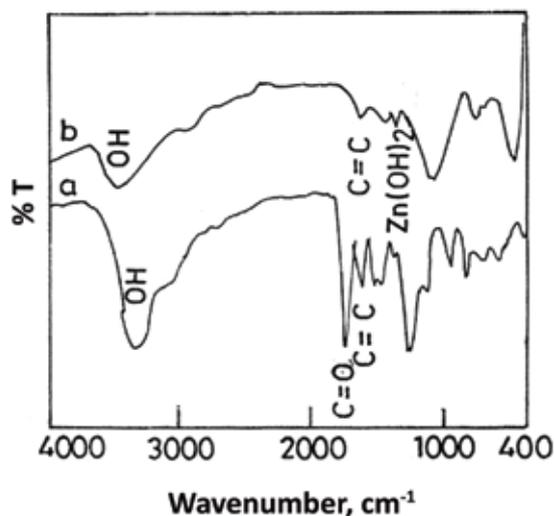


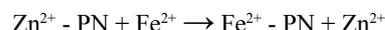
Figure 3. FTIR spectra (KBr) of pure PN (a) and of film formed on the surface of the metal immersed in test solution (b)
 (a) pure PN
 (b) PN (60 mg/L) + Zn^{2+} (50 mg/L)

3.10 Proposed mechanism of corrosion inhibition

With these discussions, a mechanism may be proposed for the corrosion inhibition of carbon steel immersed in well water by PN (60 mg/L) - Zn^{2+} (50 mg/L) system.

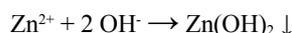
1. When the formulation consisting of 60 mg/L of PN and 50 mg/L of Zn^{2+} in well water there is formation of PN - Zn^{2+} complex in solution.
2. When carbon steel is immersed in this solution PN - Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.

3. PN - Zn^{2+} complex is converted into PN - Fe^{2+} complex on the anodic sites of the metal surface with the release of zinc ion.

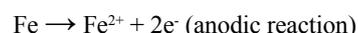


4. The released Zn^{2+} combines with OH^- to form Zn(OH)_2 on the cathodic sites of the metal surface.

5. Thus the protective film consists of PN - Fe^{2+} complex and Zn(OH)_2 .



6. In near neutral aqueous solution, the anodic reaction is the formation of Fe^{2+} . This anodic reaction is controlled by the formation of PN - Fe^{2+} complex on the anodic site of the metal surface. The cathodic reaction is the generation of OH^- which is controlled by the formation of Zn(OH)_2 on the cathodic sites of the metal surface.



7. This accounts for the synergistic effect of PN - Zn^{2+} system.

4. Conclusions

To summarize, phenolphthalein acts as a corrosion inhibitor system for carbon steel in well water. Its efficiency increased due to the transporting ability of zinc ion through the formation of the PN - Zn^{2+} complex. A suitable mechanism has been proposed for the corrosion inhibition based on the results of electrochemical studies such as polarization and AC impedance and FTIR spectra. Perusal of the spectral analysis suggests that the protective film consists of Fe^{2+} - PN complex at the anodic sites and Zn(OH)_2 at the cathodic sites on the metal surface, which confirms that PN - Zn^{2+} system functions as a mixed inhibitor system.

5. Acknowledgement

The authors are thankful to their management and University Grants Commission, India for help and encouragement.

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