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Corrosion Inhibition by Amino Trimethylene Phosphonic Acid (ATMP) - Zn^{2+} System for Carbon Steel in Ground Water

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Abstract

The inhibition efficiency (IE) of Amino Trimethylene phosphonic acid (ATMP) in controlling corrosion of carbon steel immersed in ground water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. It is observed that the synergistic formulation consisting of 250 ppm ATMP and 10 ppm of Zn^{2+} has 98% IE. Polarization study reveals that ATMP-Zn^{2+} system functions as a cathodic inhibitor system. AC impedance study reveals that a protective film is formed on the metal surface.

Keywords*:* carbon steel, corrosion inhibition, synergistic effect, cathodic inhibitor, phosphonic acid.

Introduction

The usage of ground water is common in all industries. The role of dissolved oxygen in ground water is the predominant factor to cause mild steel corrosion [1-2]. Depending upon the metal/environment combinations, different types of inhibitors are used in suitable concentrations. Speller [3-5] reported that "Compound films" formed by phosphate – chromate mixture are more effective than those of either alone. The synergistic effect of halides and organic compound inhibitors are reported often in the literature [6-9]. Several inhibitors such as phosphonic acid [10-11], thiourea [12], carboxy methyl cellulose [13],

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and sodium dodecyl sulphate [14] have been used to control corrosion of carbon steel. Inhibitors for carbon steel in near neutral aqueous solutions are soluble chromates, dichromates nitrates, borates, benzoates and salts of carboxylic acids. Corrosion inhibition due to the formation of oxide layer on Cu metal surface in concentrated propionic acid and dilute citric acid [15] has been reported. The corrosion inhibition of carbon steel in ground water by adipic acid and Zn^{2+} system has been reported [16]. Existence of synergism between succinic acid and Zn^{2+} in controlling corrosion of carbon steel in well water has been investigated [17]. Inhibitors such as benzoate, phthalate and other carboxylates [18-20] stabilize the oxide film on iron surface; presumably, their inhibitive action results from the bonding of the O^- ion. Carboxylates are anodic inhibitors. The corrosion inhibition of steel by salicylic acid in acidic media has been investigated [21]. In the present study, synergistic effect of AminoTrimethylene phosphonic acid ATMPand Zn^{2+} in corrosion inhibition of carbon steel in ground water has been investigated in detail. Amino Trimethylene phosphonic acid is an environment friendly organic compound, $C_3H_{12}P_3O_9N$, which is mainly used in open water circulation cooling system, petroleum pipelines and boilers. While the inhibition efficiencies have been evaluated by weight loss method, the mechanistic aspects are based upon the results of potentiostatic polarization and AC impedance studies.

Experimental

Preparation of the specimens

Carbon steel specimens (0.025% S, 0.06% P, 0.4% Mn, 0.15% C and the rest iron) of the dimension 1.0 x 4.0 x 0.2 cm were polished to a mirror finish and degreased with trichloro ethylene and used for the weight loss method and surface examination studies. Ground water was collected from Vadipatty village near Kodai road, Tamilnadu, India.

Weight loss method

The parameters of ground water used in the present study are given in Table 1. Carbon steel specimens in triplicate were immersed in 100 mL of ground water containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} for five days. The weights of the specimens before and after immersion were determined using a balance Shimadzu AY62 model. The corrosion products were cleaned with Clarke's solution [22]. The inhibition efficiency (IE) was then calculated using the equation

$$IE = 100\ [1-(w_2/w_1)]\ \%$$

where w_1 and w_1 are the corrosion rates (mdd) in absence and presence of inhibitor, respectively.

Potentiostatic polarization study

This study was carried out using CHI 66A Electrochemical Workstation model. A three-electrode cell assembly was used. The working electrode used was as a

rectangular specimen of carbon steel with its faces with a constant exposed area of 1 cm^2. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrode. The results such as Tafel slopes, I_{corr} and E_{corr} were calculated.
Tangents were drawn on the cathodic and anodic polarization curves. From the point of intersection of the two tangents, I_{corr} and E_{corr} were calculated.

Table 1. Parameters of ground water used is the present investigation.

Parameter	Value
pH	8.0
TDS	810 mg/L
Alkalinity	389 mg/L
Chloride	15 mg/L
Sulphate	17 mg/L
Calcium	82 mg/L
Magnesium	92 mg/L
Barium	14mg/L

AC impedance measurements
The CHI 66A Electrochemical Workstation model was used for AC impedance measurements. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated.

Results and discussion
Parameters of ground water
Corrosion behaviour of carbon steel in ground water was evaluated and the various parameters of ground water are given in Table 1.

Analysis of the results of weight loss method

Table 2. Corrosion rates (CR) of carbon steel in ground water in the presence of the inhibitor system and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor system: ATMP + Zn^{2+} (0 ppm); immersion period: 5 days.

ATMP/ppm	Zn^{2+}/ppm	CR/mdd	IE/%
0	0	13.64	--
50	0	6.55	52
100	0	6.14	55
150	0	4.09	70
200	0	3.55	74
250	0	2.73	80

Table 3. Corrosion rates (CR) of carbon steel in ground water in the presence of the inhibitor system and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor system: ATMP + Zn^{2+} (5 ppm); immersion period: 5 days.

ATMP/ppm	Zn^{2+}/ppm	CR/mdd	IE/%
0	5	13.64	--
0	5	15.00	-10
50	5	6.82	50
100	5	6.14	55
150	5	2.73	80
200	5	2.05	85
250	5	3.0	78

Table 4. Corrosion rates (CR) of carbon steel in ground water in the presence of the inhibitor system and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor system: ATMP + Zn^{2+} (10 ppm); immersion period: 5 days.

ATMP/ppm	Zn^{2+}/ppm	CR/Mdd	IE/%
0	0	13.64	--
0	10	12.96	5
50	10	2.05	85
100	10	2.59	81
150	10	6.14	55
200	10	4.77	65
250	10	0.27	98

Table 5. Corrosion rates (CR) of carbon steel in ground water in the presence of the inhibitor system and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor system: ATMP + Zn^{2+} (25 ppm); immersion period: 5 days.

ATMP/ppm	Zn^{2+}/ppm	CR/mdd	IE/%
0	0	13.64	--
0	25	12.28	10
50	25	5.45	60
100	25	1.36	90
150	25	4.09	70
200	25	4.77	65
250	25	2.73	80

Table 6. Corrosion rates (CR) of carbon steel in ground water in the presence of the inhibitor system and the inhibition efficiency (IE) obtained by weight loss method. Inhibitor system: ATMP + Zn^{2+} (50 ppm); immersion period: 5 days.

ATMP/ppm	Zn^{2+}/ppm	CR/mdd	IE/%
0	0	13.64	--
0	50	12.00	12
50	50	3.41	75
100	50	2.45	82
150	50	0.27	98
200	50	0.27	98
250	50	1.77	87

The inhibition efficiencies (IE) of ATMP in controlling corrosion of carbon steel in ground water, for a period of five days in the absence and presence of Zn^{2+}, obtained by weight loss method are given in Tables 2 to 6. ATMP alone has 80% IE, whereas Zn^{2+} has 5% IE. In the absence of ATMP, the rate of transport of Zn^{2+} from the bulk of the solution towards the metal surface is slow. Similar observations have already been reported by *Rajendran et al.* [23-24]. When ATMP is combined with Zn^{2+} ions it is found that the IE increases. For example, 250 ppm ATMP has only 80% IE and 10 ppm of Zn^{2+} has only 5%. Interestingly their combination shows 98% IE. This suggests a synergistic effect between ATMP and Zn^{2+} ions; ATMP is able to transport Zn^{2+} towards the metal surface.

Analysis of the results of potentiostatic polarization study for the ATMP-Zn^{2+} system

Polarization study has been used to investigate the protective film formed on the metal surface [25-31].

The corrosion parameters of carbon steel immersed in various test solutions obtained by polarization study are given in Table 7.

Table 7. Corrosion parameters obtained by potentiostatic polarization method.

System	E_{corr}/ /(mV vs. SCE)	I_{corr}/ /(A/cm^2)	b_a/ /(mV/decade)	b_c/ /(mV/decade)
Ground water	-410	5.2 x 10^{-5}	208	335
Ground water + Zn^{2+} 10 ppm + ATMP 250 ppm	-460	3.8 x 10^{-5}	220	298

The polarization curves are shown in Fig. 1.

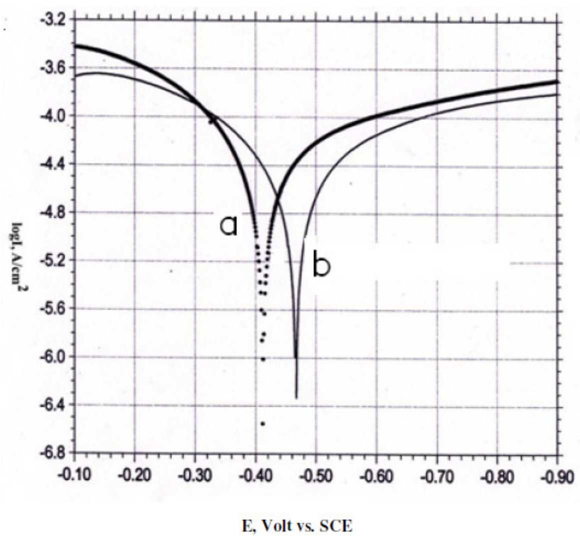


Figure 1. Polarization curves of carbon steel immersed in various test solutions. a) Ground water; b) ground water + Zn^{2+} 50 ppm + ATMP 250 ppm.

When carbon steel is immersed in ground water, the corrosion potential is – 410 mV vs. saturated calomel electrode (SCE). The formulation consisting of 250 ppm of ATMP and 50 ppm of Zn^{2+} shifts the corrosion potential to -460 mV vs. SCE. This suggests that the cathodic reaction is controlled predominantly, which is further conformed by more shifted in the cathodic Tafel slope as shown in Table 7. This result suggests that the ATMP– Zn^{2+} formulation functions as a cathodic inhibitor. The corrosion current for ground water is 5.2 x 10^{-5} A/cm^2. It is decreased to 3.8 x 10^{-5} A/cm^2 by the 250 ppm of ATMP and 50 ppm of Zn^{2+} system. This indicates that a protective film is formed on the metal surface and the electron transfer from the metal surface is prevented.

Analysis of the results of AC impedance spectra

AC impedance spectra have been used to investigate the formation of a protective film on the metal surface [32-40].The AC impedance spectra of carbon steel in various solutions are shown in Fig. 2. The AC impedance parameters, namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 8. When carbon steel is immersed in ground water, R_t value is 386 Ω cm^2 and C_{dl} value is 1.32 x 10^{-8} F cm^{-2}. When ATMP and Zn^{2+} are added to ground water, R_t value increases from 386 Ω cm^2 to 509 Ω cm^2. The C_{dl} decreases from 1.32 x 10^{-8} Fcm^{-2} to 1.00 x 10^{-8} μFcm^{-2}. This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of ATMP– Zn^{2+} system. Equivalent circuit diagram for such a system is shown in scheme 1.

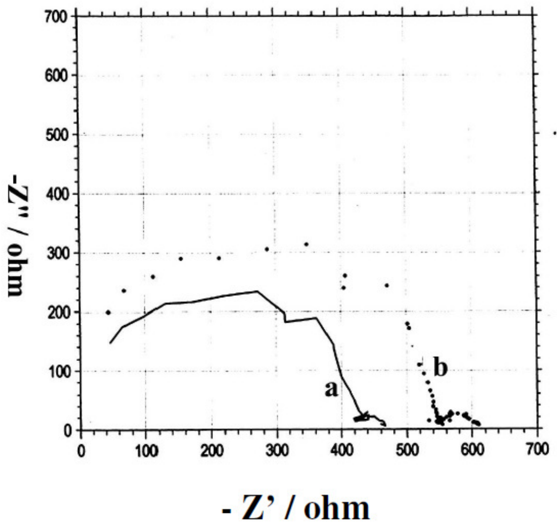
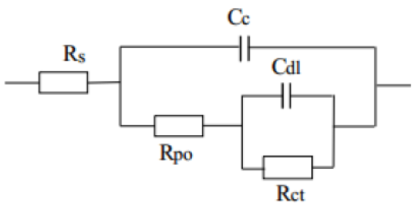


Figure 2. AC impedance spectra of carbon steel immersed in various test solutions. a) Ground water; b) ground water + Zn^{2+} 10 ppm + ATMP 250 ppm.

Table 8. Corrosion parameters obtained by AC impedance studies.

System	R_t/Ω cm^2	C_{dl}/F cm^{-2}
Ground water	386	1.32×10^{-8}
Ground water + Zn^{2+} 10 ppm + ATMP 250 ppm	509	1.00×10^{-8}



Scheme 1. Equivalent circuit for a failed coating. C_c - Capacitance of the intact coating; R_{po} - Pore resistance; R_{ct} - Charge transfer resistance; R_s – Solution resistance; C_{dl} – Double layer capacitance.

Mechanism of corrosion inhibition

The results of the weight loss study show that the formulation consisting of 250 ppm of ATMP and 50 ppm of Zn^{2+} has 98% IE in controlling corrosion of carbon steel, in ground water. A synergistic effect exists between Zn^{2+} and ATMP. Polarization study reveals that this formulation functions as a cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface.

a) When the solution containing ground water, 50 ppm of Zn^{2+} and 100 ppm of ATMP is prepared, there is formation of Zn^{2+}-ATMP complex in solution.
b) When carbon steel is immersed in the solution, the Zn^{2+}-ATMP complex diffuses from the bulk of the solution towards the metal surface.
c) On the metal surface, Zn^{2+} – ATMP complex is converted into Fe^{2+} – ATMP complex on the anodic sites. Zn^{2+} is released.
d) Zn^{2+}-ATMP+ Fe^{2+} → Fe^{2+} – ATMP+ Zn^{2+}
e) The released Zn^{2+} combines with OH^- forming $Zn(OH)_2$ on the cathodic sites.
f) $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$
g) Thus the protective film consists of Fe^{2+} – ATMP complex and $Zn(OH)_2$.

Conclusions

The present study leads to the following conclusions:

- a synergistic effect exists between Amino Trimethylene Phosphonic acid (ATMP) and Zn^{2+} in controlling the corrosion of carbon steel immersed in ground water;
- the formulation consisting of 250 ppm of ATMP and 10 ppm of Zn^{2+} has 98% IE;
- polarization study reveals that ATMP–Zn^{2+} system functions as a cathodic inhibitor system;
- AC impedance spectra reveal that a protective film is formed on the metal surface.

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