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Effect of inhibitors and biocide on corrosion control of mild steel in natural aqueous environment

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Abstract

A triazole phosphonate compounds, namely, 3-benzyledene amino 1,2,4-triazole phosphonate (BATP), 3-cinnamyledene amino 1,2,4-triazole phosphonate (CATP) and 3-anisolidene amino 1,2,4-triazole phosphonate (AATP), were synthesized and its inhibition efficiency along with biocide action on corrosion of mild steel in natural aqueous solution was investigated through weight loss and electrochemical polarization techniques. Results from experimental observation have indicated AATP as a better corrosion inhibitor for mild steel in aqueous solution. Additionally, the formulation consisting of AATP, Mo and CTAB offered good corrosion inhibition efficiency. Surface characterization studies were carried out to establish the mechanism of corrosion inhibition of mild steel in aqueous media.

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Keywords: Corrosion; Mild steel; Triazole; Biocide

1. Introduction

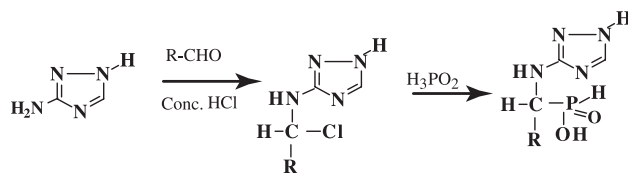
Mild steel is employed widely in most industries in due of low cost and its availability in ease for the fabrication of various reaction vessels such as cooling tower tanks, pipelines, etc. Fouling and corrosion are the two important operational discrepancies in heat exchangers and associated cooling water system pipelines. The problems include flow blockage of pipes, pipe punctures and unacceptable corrosion rates of the

system components. For controlling fouling and corrosion, continuous addition of inhibitors as well as the addition of biocides every week or once in a fortnight is explored. Hence, the phenomenon of studying the effect of inhibitors and biocides is quite essential.

Organic substances employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms, such as nitrogen, oxygen, sulphur and phosphorus, multiple bonds or aromatic rings, and block the active sites, thus decreasing the corrosion rate [1–4]. Generally, chlorine or hypochlorites are used as biocides in aqueous environments for the prevention of biofouling, microbial corrosion and/or other microbial metabolic activities of microorganisms on metal surface, which directly influence corrosion process [5,6]. Excess dissolved chlorine in

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R- Benzaldehyde, Cinnamaldehyde and Anisaldehyde

Scheme 1.

water, however, creates corrosive environment and gaseous chlorine itself is more dangerous. Due to strong oxidizing tendency, hypochlorite has strong accumulation storage problem.

Phosphonic acids are noted for their hydrolytic stability, scale-inhibiting property and ability to form complexes with metal cations. Thus, they have been widely used as corrosion inhibitors [7–10]. Hence, in the present investigation, some triazole derivatives are synthesized that contains phosphonic

acid group, and their efficiency in the inhibition of mild steel corrosion in neutral aqueous environment is studied.

In the present study, 3-benzylidene amino 1,2,4-triazole phosphonate (BATP), 3-cinnamylidene amino 1,2,4-triazole phosphonate (CATP) and 3-anisalidene amino 1,2,4-triazole phosphonate (AATP) were used as inhibitor, while biocide, cetyl trimethyl ammonium bromide (CTAB) is used to study their interference effect on corrosion process.

Name	Abbreviation	Structure
3-Benzylidene amino 1,2,4-triazole phosphonate	BATP	
3-Cinnamylidene amino 1,2,4-triazole phosphonate	CATP	
3-Anisalidene amino 1,2,4-triazole phosphonate	AATP	

Fig. 1. Name and structure of the compounds.

2. Experimental

2.1. Synthesis of triazole derivatives

All the tested azoles were synthesized [11–13] in the laboratory by condensing 3-amino 1,2,4-triazole, hypophosphorus acid with benzaldehyde, cinnamaldehyde and anisaldehyde (Scheme 1). The synthesized compounds were characterized by their IR and NMR spectra. The structures of the compounds are given in Fig. 1.

2.2. Sample preparation

Mild steel specimens of following compositions were used for the experiment: C—0.13%, P—0.032%, Si—0.014%, S—0.025%, Mn—0.48% and Fe—balance. Prior to each experiment, the specimens were polished with 200–800 grades SiC emery paper. Then the specimen was washed several times with distilled water, degreased in acetone and dried. The specimen area of $4 \times 2 \text{ cm}^2$ was used for weight loss measurements and 1 cm^2 test area for polarization studies.

2.3. Weight loss experiments

Initial weight of the mild steel specimen before corrosion test was measured. Mild steel specimens in triplicate were immersed in the test solution for 3 days. After 3 days, specimens were removed, then washed in water, acetone and, finally, dried in air. The loss in weight was determined and their efficiencies were assessed in the systems in Table 1.

Table 1

System	Material used	Medium	Parameters of interest
System I	BATP, CATP, AATP with Mo	lake water	Inhibition efficiency
System II	CTAB	lake water	Biocide efficiency
System III	BATP, CATP, AATP with Mo (inhibitors), CTAB (biocide)	lake water	Interference in the inhibitors and biocide (Inhibitors and biocide are added at same time)
System IV	BATP, CATP, AATP with Mo (inhibitors), CTAB (biocide)	lake water	Biocide are added first, after 24 h inhibitors were added

2.4. Potentiodynamic polarization measurement

Potentiodynamic polarization studies were carried out using Vibrant Potentiostat/Galvanostat model no. VSM/CS/30. A platinum electrode and saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. The working electrodes constitute mild steel specimens of 1 cm^2 of test area. All the experiments were carried out at constant temperature of $300 \pm 2 \text{ K}$ with natural lake water as an electrolyte. Polarization studies were carried out in lake water containing various concentrations of additives (systems I to IV).

2.5. Surface examination study

The mild steel specimens immersed in various test solutions for a period of 10 days. After 10 days, the specimens were taken out and dried. The nature of the film formed on the surface on the metal specimens was analysed by the various surface analytical techniques.

The Fourier transforms infrared spectra (FT-IR) spectra were recorded in a Perkin-Elmer 1600 FT-IR spectrophotometer. XRD patterns of the film formed on the metal surface were recorded using a computer controlled X-ray powder diffractometer, JEOL JDX with $\text{CuK}\alpha$ (Ni-filtered) radiation ($\lambda = 1.5418 \text{ \AA}$) at a rating of 40 kV, 20 mA.

3. Results and discussions

3.1. Weight loss measurement

The corrosion rate of mild steel in lake water with the presence of inhibitors and biocides are presented in Table 2.

3.1.1. Inhibitors on corrosion (system I)

Influence of inhibitor on corrosion is presented in Table 2. BATP, CATP and AATP were slightly inhibiting corrosion and the inhibition efficiency was about 46%, 50% and 57%, respectively. While adding Mo, all the phosphonate showed an increased efficiency.

3.1.2. Biocides on corrosion (system II)

The tested biocide showed corrosion inhibition in the range of 52%.

Table 2

Corrosion rate of mild steel in lake water in the presence of optimum concentrations of inhibitors and biocide (systems I–IV)—weight loss method

Inhibitor	System	Concentration of inhibitor (ppm)	Corrosion rate (mpy)	Inhibition efficiency (%) (I.E.)
Blank		–	13.45	–
BATP		4	7.14	46.91
CATP		4	6.72	50.03
AATP		3	5.76	57.17
Molybdenum	System I	5	6.67	50.40
BATP+Mo		4+5	6.29	53.23
CATP+Mo		4+5	5.96	55.68
AATP+Mo		3+5	4.90	63.56
CTAB	System II	15	6.33	52.93
BATP+Mo+CTAB		4+5+15	3.79	71.82
CATP+Mo+CTAB	System III	4+5+15	3.68	72.63
AATP+Mo+CTAB		3+5+15	2.62	80.52
CTAB+BATP+Mo		15+4+5	4.65	65.42
CTAB+CATP+Mo	System IV	15+4+5	4.63	65.57
CTAB+AATP+Mo		15+3+5	3.17	76.43

3.1.3. Biocide and inhibitors on corrosion (systems III and IV)

In system III, inhibitors (BATP, CATP and AATP with Mo) and biocide were added at the same time

and corrosion efficiency was calculated and listed in Table 2. In the presence of CTAB with inhibitor (BATP, CATP and AATP), the efficiency was about 71.82%, 72.63% and 80.52%, respectively.

In system IV (Table 2), after killing of bacteria by biocide, in the presence of AATP, the corrosion inhibition was about 76.43%. While adding BATP and CATP, the inhibition efficiencies were about 65.42% and 65.57%, respectively.

3.2. Electrochemical study

The potentiodynamic polarization parameters of mild steel immersed in lake water for all three systems are given in Table 3 and corresponding polarization curves are also shown in Figs. 2–4. Additions of 4 ppm of BATP, CATP and AATP to the tested solution showed a shift in corrosion potential towards active direction corresponding to the predominant control cathodic reaction. Addition of Mo controls both cathodic as well as anodic reaction. However, along with inhibitor, they also predominantly control the cathodic reaction site. In system III, the corrosion potential shifted to noble direction indicating the dominance of BATP, CATP and AATP on the control over both cathodic, anodic reaction site, thus accounting for the decreased corrosion rate. In system III, the inhibition efficiency of BATP, CATP and AATP was about 83.69%, 84.61% and 93.53%. The higher inhibition efficiency shown by AATP compared to

Table 3

Potentiodynamic polarization parameters of mild steel in lake water with and without inhibitor and biocide (systems I–IV)

Compounds	System	OCP (mV vs. SCE)	E_{corr} (mV)	I_{corr} (mA/cm ²) × 10 ⁻³	Corrosion rate (mpy)	Efficiency (I.E.) (%)
Blank	–	– 690	– 695	32.5	14.88	–
BATP	System I	– 720	– 734	12.0	5.49	63.07
CATP	System I	– 736	– 740	12.0	5.49	63.07
AATP	System I	– 756	– 810	4.8	2.19	85.23
BATP+Mo	System I	– 820	– 770	7.4	3.38	77.23
CATP+Mo	System I	– 574	– 769	7.8	3.57	76.00
AATP+Mo	System I	– 510	– 804	4.5	2.05	86.15
BATP+Mo+CTAB	System III	– 733	– 764	5.3	2.42	83.69
CATP+Mo+CTAB	System III	– 723	– 745	5.0	2.28	84.61
AATP+Mo+CTAB	System III	– 665	– 654	2.1	0.99	93.53
CTAB+BATP+Mo	System IV	– 733	– 727	8.5	3.89	73.84
CTAB+CATP+Mo	System IV	– 685	– 680	8.4	3.84	74.15
CTAB+AATP+Mo	System IV	– 700	– 682	2.8	1.32	91.38

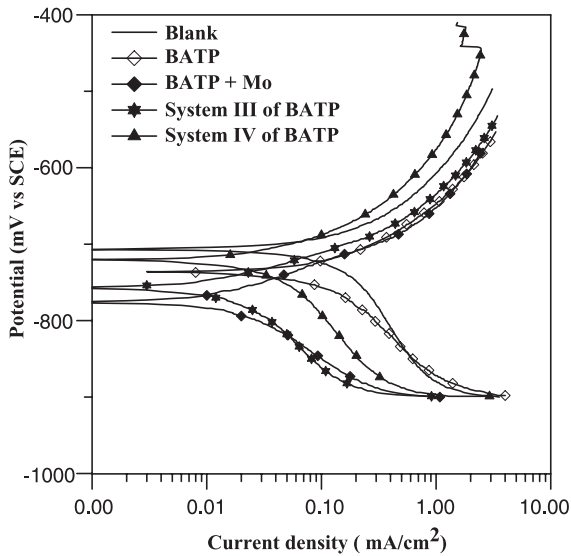


Fig. 2. Potentiodynamic polarization curves of mild steel in lake water with and without BATP and biocide.

others may attributed to the increased electron density leading to electron transfer mechanism from functional group to metal surface, producing greater coordinate bonding with a greater adsorption. Similar explanation has been delivered in the classical work

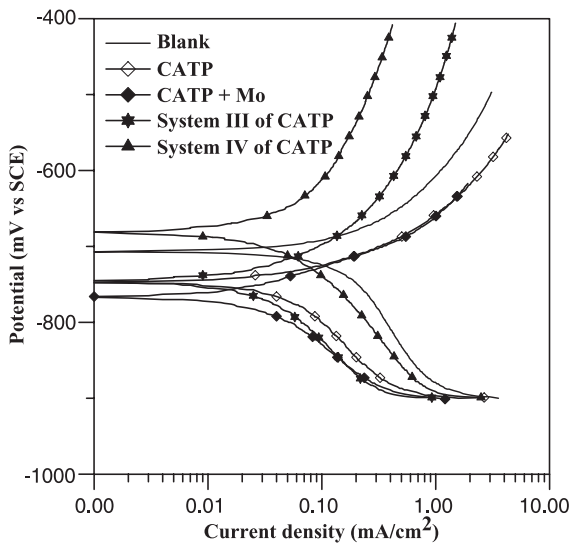


Fig. 3. Potentiodynamic polarization curves of mild steel with different system of CATP.

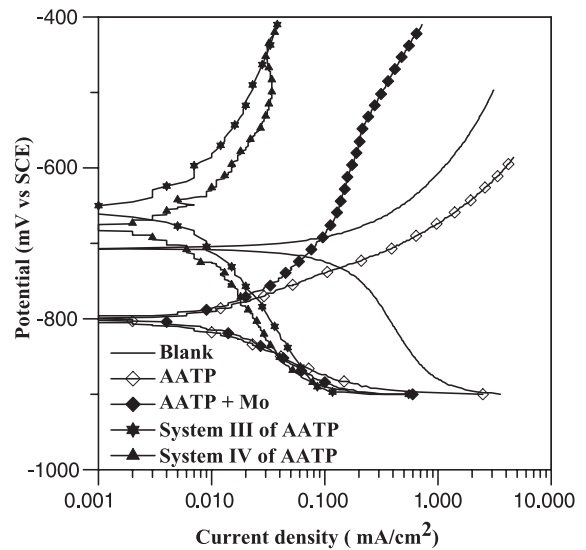


Fig. 4. Potentiodynamic polarization curves of mild steel with different system of AATP.

of Khamis et al. [14]. When inhibitors and biocide were simultaneously injected, the bacterial killing efficiency was found beneficial.

From the polarization curves, the corrosion current density (i_{corr}) was determined by Tafel extrapolation method and the corrosion rates were determined from i_{corr} values. The corrosion current density was decreased considerably in the presence of inhibitor. The value of corrosion rate of mild steel in the presence of inhibitor was much smaller than that in the absence of an inhibitor. In system IV, the corrosion inhibition efficiency was lower compared to system III (Table 3). In the presence of AATP, the efficiency was about 91.38% and OCP was -700 mV. The inhibition efficiency of BATP and CATP (system IV) was about 73.84% and 74.15%, respectively. It was observed from the results that the combination of BATP, CATP and AATP with molybdenum acted as good inhibitor. Besides, in system III, the inhibitor recorded higher efficiencies than system IV and indicates the interference between biocide and inhibitors system.

3.3. Analysis of FT-IR spectra

FT-IR of AATP and CTAB are presented in Fig. 5a and b. The stretching mode of P=O bond gives rise to

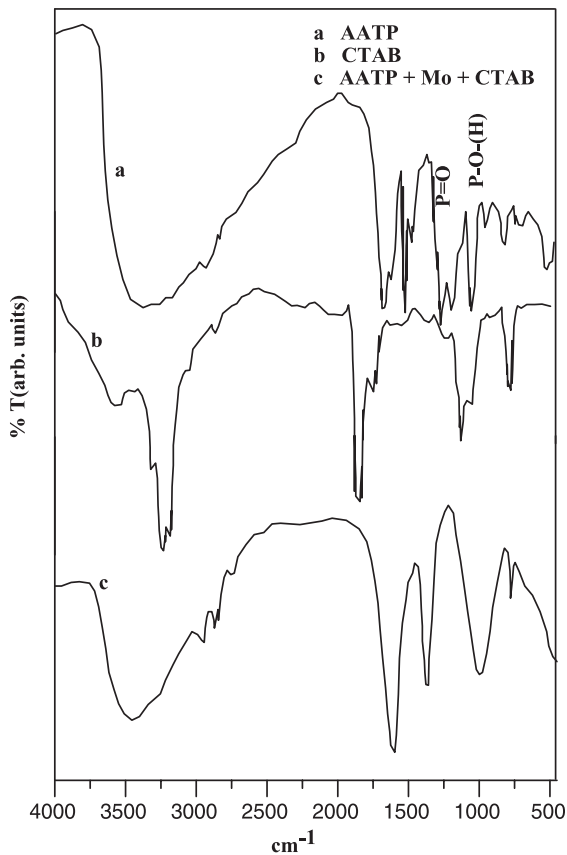


Fig. 5. Infrared transmission spectra of (a) AATP, (b) CTAB infrared reflection–absorption spectrum of the film formed on the mild steel substrate after immersion in the solution containing (c) mixture of SATP+Mo+CTAB.

a strong band in the region $1380\text{--}1140\text{ cm}^{-1}$ as expected. The two prominent bands at 1249 and 948 cm^{-1} were attributed to the PO_3H_2 group of the molecule. The band at 1249 cm^{-1} is assigned to the P–O stretch of the ionic species and the other at 948 cm^{-1} is assigned to the P–OH stretch [15]. The reflectance absorption spectra of the film formed on mild steel immersed in the environment consisting of 4 ppm of AATP+5 ppm of Mo+15 ppm of CTAB are given in Fig. 5c. By comparison with Fig. 5a, the band at 948 cm^{-1} almost disappeared in Fig. 5c. This result are interpreted by the interactions free $\text{P}^+\text{--O}^-$ with metallic species to form P–O–M bond. Carter et al. [16] found that IR spectra obtained with an organic phosphonate in a steel substrate are consistent with the phosphate reaction on steel to produce a metal salt.

This suggests that phosphonates are coordinated with Fe^{2+} , resulting in the formation of Fe^{2+} -phosphonate complex on metal surface.

The FT-IR spectrum of pure CTAB is given in Fig. 5b. The absorption band due to vs. CH_2 appears at 2854 cm^{-1} . The aliphatic C–H stretches cause absorption at 2923 and 2854 cm^{-1} . The band at 1126 cm^{-1} corresponds to C–N stretching. The bands at 2923 and 2854 cm^{-1} suggest the presence of CTAB on the metal surface as Fe^{2+} -CTAB complex formed on the anodic sites of the metal [17].

In addition to the metal-inhibitor complex, the CTAB- Fe^{2+} complex will also deposit as a layer on

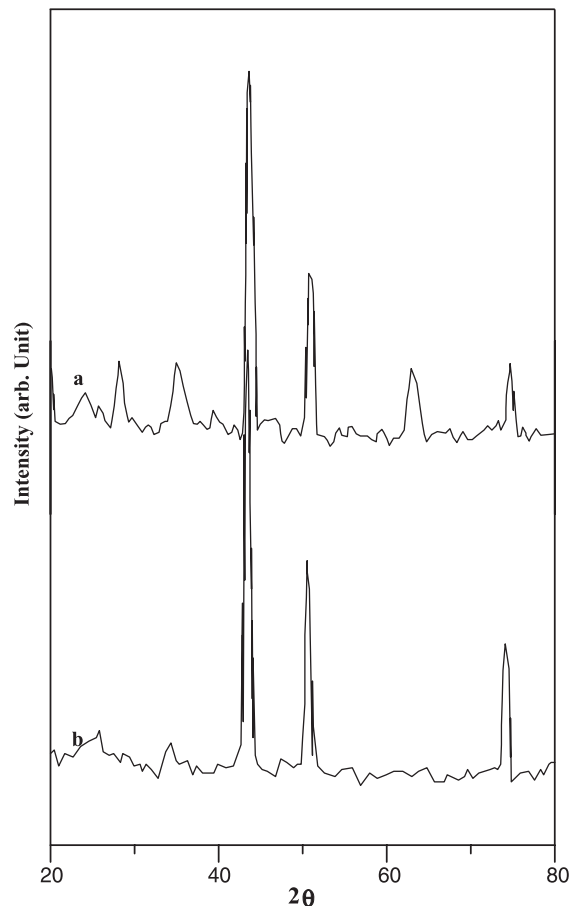


Fig. 6. XRD pattern obtained on the surface film formed on mild steel at the end of 30 days in different environment. Curves: (a) Blank, (b) AATP+Mo+CTAB.

Table 4
Bacterial density of lake water in various systems for 24 h

System	Concentration (ppm)	Bacterial count (cfu/ml)
Control	–	1.86×10^6
AATP	3	1.62×10^6
CTAB	15	5.2×10^2
AATP+Mo+CTAB	3+5+15	1.50×10^6

the metal and as a part of the protective film. From the inhibition characteristics, it supplements the corrosion-inhibiting capability of the Fe-inhibitor complex, probably through the formation of more impervious films.

3.4. Analysis of X-ray diffraction patterns

The X-ray diffraction patterns of the film formed on surface of the mild steel specimens immersed in various test solutions are given in Fig. 6. The peak due to iron appears at $2\theta = 43.8^\circ$, 50.9° and 74.5° . Peaks at $2\theta = 30.4^\circ$, 36° and 62.4° can be assigned to oxides of iron. Thus, it is observed that the surface of the metal immersed in groundwater contains iron oxides of Fe_3O_4 and FeOOH .

The XRD pattern of the surface of the alloy immersed in the solution containing 3 ppm AATP + 5 ppm Mo + 15 ppm CTAB is given in Fig. 6b. It is observed that the peaks due to oxide of iron, such as Fe_3O_4 and $\Gamma\text{-FeOOH}$, are found to be absent and the peaks due to iron alone are observed at $2\theta = 43.6^\circ$, 50.7° and 74.3° . It is inferred from the pattern that oxides of iron, such as FeOOH and Fe_3O_4 , were absent on the metal surface.

3.5. Bacterial killing efficiency

The bacterial killing efficiency of inhibitors along with biocide is presented in Table 4. In the presence of CTAB, the bacterial count was measured as 5.2×10^2 and CTAB acts as effective biocide by disturbing the arrangements of phospholipid molecules in the bacterial cell. When biocides and inhibitors were simultaneously injected, the bacterial killing efficiency was found to be little. The present investigation has clearly shown that CTAB and inhibitor combination acts as good system for bacterial control as well as corrosion control.

4. Conclusions

The conclusions drawn from the results may be given as

- All the three compounds are predominantly control cathodic reaction.
- From corrosion point of view, B ATP, C ATP and AATP with Mo act as a good inhibitor system.
- The formulations (3 ppm AATP, 5 ppm Mo and 15 ppm CTAB) had 93.53% corrosion inhibition efficiency.
- Corrosion inhibition may arise from the formation of protective film consisting of Fe^{2+} -phosphonic acid complex.

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