Contributed papers

Corrosion inhibition by ATMP-molybdate-Zn^{2+} system in low chloride media

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Abstract

The effect of amino (trimethylene phosphonic acid), (ATMP), molybdate and Zn^{2+} on the inhibition of corrosion of mild steel in a neutral aqueous environment containing 60 ppm Cl^- has been evaluated by the weight - loss method. It is found that the formulation consisting of 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} has 96 per cent inhibition efficiency. The nature of the protective film has been analysed by X-ray diffraction technique FTIR and luminescence spectra. It seems that the protective film consists of $Fe_2(MoO_4)_3$, $ZnMoO_4$, Fe^{2+}-ATMP complex and $Zn(OH)_2$. This film is found to be luminescent.

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Introduction

Several phosphonic acids have been used as corrosion inhibitors due to their ability to form complexes with metal ions, their hydrolytic stability and scale inhibiling property (Breske, 1977; Du Thanbao *et al.*, 1997; Fang *et al.*, 1993; Galkin *et al.*, 1996; Gunasekaran *et al.*, 1997; Hatch and Ralston, 1972; Horvath *et al.*, 1994; Hwa, 1969; Kubicki *et al.*, 1988; Kuznetsov, and Bardasheva, 1988; Rajendran *et al.*, 1995; 1996a; 1996b; 1996c; Sekine and Kirakawa, 1986). They show synergistic effect with several chemicals such as zinc (Gunasekaran *et al.*, 1997; Hatch and Ralston, 1972; Kubicki *et al.*, 1988; Kuznetsov, and Bardasheva, 1988; Rajendran *et al.*, 1995; 1996a; 1996b; 1996c; Sekine and Kirakawa, 1986), molybdate (Breske, 1977; Rajendran *et al.*, 1996c), carboxylic acids (Kubicki *et al.*, 1988) and dichromate (Hatch and Ralston, 1972; Hwa, 1969).

In the present work, the effect of amino (trimethylene phosphonic acid) (ATMP), molybdate and Zn^{2+} on the inhibition of corrosion of mild steel in neutral aqueous environment containing 60 ppm Cl^- has been evaluated by the weight-loss method. Potentiostatic polarisation study has been used to determine the nature of the inhibitor – whether anodic, cathodic or mixed. The nature of the inhibitive film has been analysed by X-ray diffraction (XRD) technique FTIR and luminescence spectra.

Experimental

Preparation of the specimens

Mild steel specimens (0.02 to 0.03 per cent S, 0.03 to 0.08 per cent P, 0.4 to 0.5 per cent Mn, 0.1 to 0.2 per cent C and the rest iron) of the dimensions $1 \times 4 \times 0.2$ cm were

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polished to mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies. For potentiostatic polarisation studies, mild steel rod encapsulated in Teflon with an exposed cross section of 0.5 cm diameter was used as the working electrode. Its surface was polished to mirror finish and degreased with trichloroethylene.

Weight-loss method
Mild steel specimens, in triplicate, were immersed in 100 ml of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+}, or a period of seven days. The weights of the specimens before and after immersion were determined using Mettler balance, AE-240.

Potentiostatic polarisation study
This study was carried out in a three electrode cell assembly connected to Bioanalytical system (BAS - 100A) electrochemical analyser, provided with IR compensation facility, using mild steel as the working electrode, platinum as the counter electrode and saturated calomel electrode as the reference electrode.

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

The FTIR spectra
The FTIR spectra were recorded using Perkin-Elmer 1600 FTIR spectrophotometer.

X-ray diffraction technique
The XRD patterns of the film formed on the metal surface were recorded using a computer controlled X-ray powder diffractometer, JEOL JDX 8030 with CuK_α (Ni-filtered) radiation ($\lambda = 1.5418$) at a rating of 40 kV, 20 mA. The scan rate was 0.05-20° per step and the measuring time was 1 second per step.

Luminescence spectra
The luminescence spectra of the film formed on the metal surface were recorded using Hitachi F-4500 fluorescence spectrophotometer.

Results and discussion

Analysis of the results of the weight-loss method
Corrosion rates of mild steel immersed in neutral aqueous environments containing 60 ppm Cl^-, in the absence and presence of inhibitors, are given in Table I. The inhibition efficiencies are also given in Table I and it can be seen that while 50 ppm ATMP has 15 per cent inhibition efficiency, 50 ppm Zn^{2+} is found to be corrosive. Interestingly the formulation consisting of 50 ppm ATMP and 50 ppm Zn^{2+} has 45 per cent inhibition efficiency. This suggests the synergistic effect existing between ATMP and Zn^{2+}. The formulation consisting of 50 ppm Zn^{2+} and 300 ppm MoO_4^{2-} has 90 per cent inhibition efficiency. This indicates the synergistic effect of the $Zn2+MoO_4^{2-}$ system. It is very interesting to note that the formulation consisting of 50 ppm ATMP and 300 ppm MoO_4^{2-} has only 32 per cent. This suggests the antagonistic effect existing between ATMP and MoO_4^{2-}.

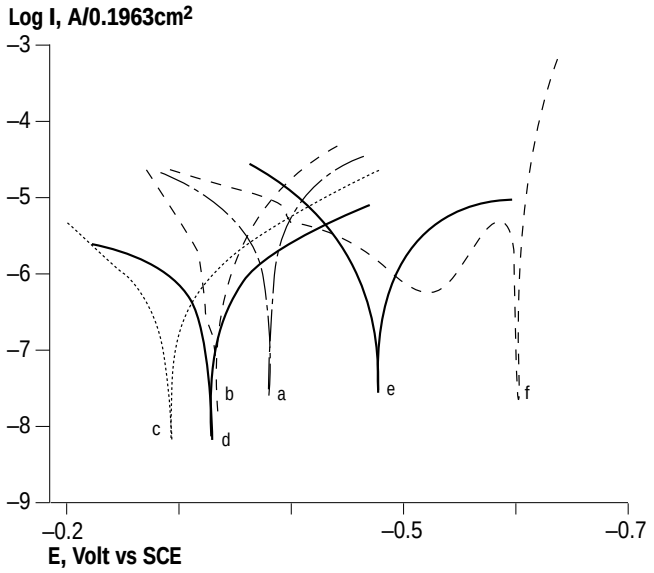
It is also inferred from Table I that the formulation consisting of 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} has 96 per cent inhibition efficiency.

Analysis of potentiostatic polarisation curves
Potentiostatic polarisation curves of mild steel immersed in various environments are given in Figure 1. It is found that ATMP alone or MoO_4^{2-} alone or the ATMP-MoO_4^{2-} system acts as anodic inhibitor. It is interesting to note that the formulation consisting of 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} shifts the corrosion potential to the cathodic side (from -389 mV us SCE to -598mV us SCE). This suggests that this formulation controls the cathodic reaction predominantly.

Table I Corrosion rates of mild steel in neutral aqueous environment (Cl^- = 60 ppm) in the absence and presence of inhibitor and the inhibition efficiencies obtained by the weight-loss method

Sample number	ATMP (ppm)	Zn^{2+} (ppm)	$Mo0_4^{2-}$ (ppm)	Corrosion rate (mdd)	Inhibition efficiency (%)
1	0	0	0	15.54	–
2	50	0	0	13.21	15
3	0	50	0	19.11	-23
4	50	50	0	8.55	45
5	0	0	300	3.11	80
6	0	50	300	1.58	90
7	50	50	300	0.62	96
8	50	0	300	10.57	32

Figure 1 Potentiostatic polarisation curves of mild steel in various environments



Key

(a) Cl^- (60ppm)

(b) Cl^- (60ppm) + ATMP (50ppm)

(c) Cl^- (60ppm) + MoO_4^{2-} (300ppm)

(d) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm)

(e) Cl^- (60ppm) + Zn^{2+}(50ppm)

(f) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm) + Zn^{2+}(50ppm)

Analysis of the XRD patterns

The XRD patterns of mild steel surfaces immersed in various environments are given in Figure 2.

The XRD pattern of the polished metal surface is given in Figure 2a. The peaks due to iron appear at 2θ = 44.8°, 65.1° and 82.4°. This suggests the absence of oxides of iron such as γ-FeOOH and Fe_3O_4 on the metal surface (Favre and Landolt, 1993). This is probably due to the very thinness of the oxide film.

The XRD pattern of the film formed on the surface of the metal immersed in the environment consisting of 60 ppm Cl^-, 50 ppm ATMP and 300 ppm MoO_4^{2-} is given in Figure 2b. The peaks at 2θ = 13.7°, 15.3°, 20.1°, 22.6°, 24.7° and 27.2° suggest the presence of iron-molybdate complex, $Fe_2(MoO_4)_3$ on the metal surface (JCPDS Nr. 200526). The peaks due to iron appear at 2θ = 44.5°, 64.9° and 82.3°.

The XRD pattern of the film formed on the surface of the metal immersed in the environment consisting of 60 ppm Cl^- 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} is given in Figure 2c.

The peaks at 2θ = 13.8°, 20.1° and 22.7° suggest the presence of $Fe2(MoO_4)_3$ complex on the metal surface (JCPDS Nr. 200526). The peak at 2θ = 30.38° is due to $ZnMoO_4$ (JCPDS Nr. 251024). The iron peaks occur at 2θ = 44.8°, 65.1° and 82.4°.

Analysis of FTIR spectra

The FTIR spectra of pure ATMP and pure sodium molybdate are given in Figures 3a and b. The FTIR spectrum of the solid iron-molybdate complex prepared by mixing ferrous sulphate solution and sodium molybdate solution is given in Figure 3c. It is observed that the Mo-O frequency decreases from 818.1cm^{-1} to 798.2cm^{-1}.

The FTIR spectrum (KBr) of the film scratched from the surface of the metal immersed in the environment consisting of 60 ppm Cl^-, 50ppm ATMP and 300ppm MoO_4^{2-} is given in Figure 3d. It is found that the Mo-O frequency is shifted from 818.1 cm^{-1} to 763.6cm^{-1}. This shift may be caused by the decrease of electron cloud density of Mo-O bond. Due to the shift of electron

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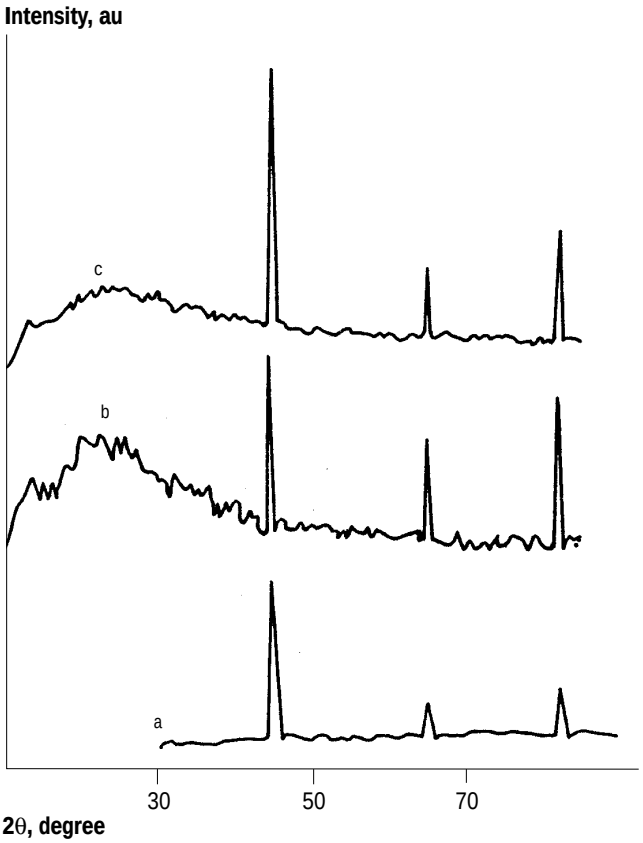
Figure 2 XRD patterns of mild steel surface immersed in various environments



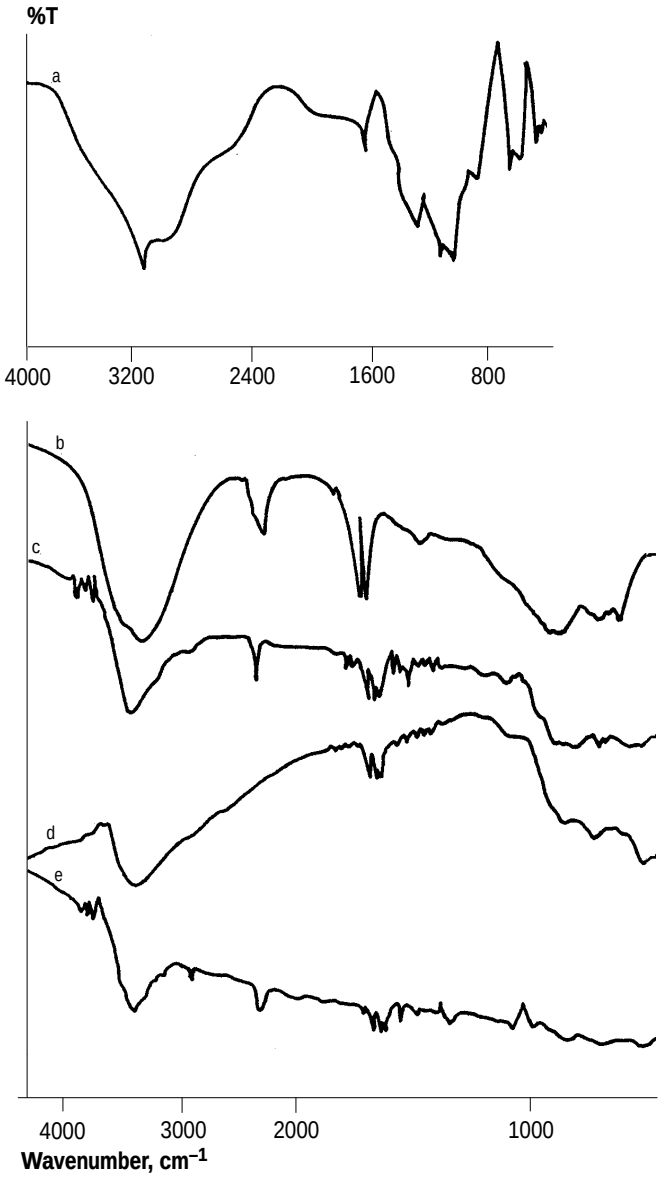
Key

(a) Polished metal

(b) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm)

(c) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm) + Zn^{2+} (50ppm)

Figure 3 FITR spectra of mild steel surface immersed in various environments



Key

(a) ATMP

(b) Na_2MoO_4

(c) Complex formed by mixing Fe^{2+} and MoO_4^{2-}

(d) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm)

(e) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm) + Zn^{2+} (50ppm)

cloud density from oxygen atom to iron, it is suggested that the oxygen atom of the molybdate anion is coordinated to iron, resulting in the formation of iron molybdate complex.

The FTIR spectrum of the film carefully scratched from the surface of the metal immersed in the environment containing 60 ppm Cl^-, 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} is given in Figure 3e. It is observed that the Mo-O frequency decreases from 818.1 cm^{-1} to 800 cm^{-1}. This suggests the presence of iron molybdate complex on the metal surface.

Further, it is observed that the P-O stretching frequency of ATMP decreases from 1,002cm^{-1} to 972.7 cm^{-1}; the C-N stretching frequency decreases from 1,145cm^{-1} to 1,066.7cm^{-1}. It is suggested that ATMP is coordinated to Fe^{2+} through O atom and N atom (Fang *et al.*, 1993, Rajendran *et al.*, 1995, 1996a, 1997c; Horner and Horner, 1976). The peak at 1,344 cm^{-1} is due to $Zn(OH)^{2-}$ (Sekine and Kirakawa, 1986).

Analysis of luminescence spectra

The emission spectra (λ_{ex} = 413 μm) of the film formed on the surface of the metal specimens immersed in various environments are given in Figures 4a and b.

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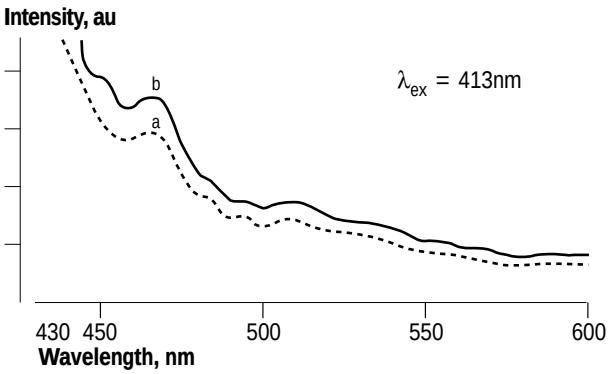
Figure 4 Luminescence spectra of mild steel surface immersed in various environments



Key

(a) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm)

(b) Cl^- (60ppm) + ATMP (50ppm) + MoO_4^{2-} (300ppm) + Zn^{2+} (50ppm)

The emission spectrum of the film formed on the surface of the metal immersed in the environment containing 60 ppm Cl^-, 50 ppm ATMP and 300 ppm MoO_4^{2-} is given in Figure 4a and that of the metal immersed in the environment consisting of 60 ppm Cl-, 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} is given in Figure 4b. They show peaks at 463 µm and 505 µm. It is very interesting to note that in the presence of Zn^{2+} there is increase in the intensity of the peaks. This suggests that the formation of protective film is enhanced in the presence of Zn^{2+}. This is in agreement with the results of the weight-loss method which reveal that in the presence of Zn^{2+} the inhibition efficiency increases from 32 to 96 per cent.

Mechanism of corrosion inhibition

The results of the weight loss method show that the formulation consisting of 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} had an inhibition efficiency of 96 per cent. The polarisation study reveals that this system controlled the cathodic reaction predominantly. The XRD pattern shows that the protective film consisted of $Fe_2(MoO_4)_3$ and $ZnMoO_4$. The FTIR spectra indicate that the protective film consisted of Fe^{2+}-ATMP complex, iron molybdate complex and $Zn(OH)_2$.

The film was found to be luminescent. In order to explain these observations in a holistic way, the following mechanism of inhibition of corrosion is proposed.

- When the environment consisting of 60 ppm Cl^-, 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} is prepared, there is formation of Zn^{2+}-ATMP complex and Zn^{2+}-MoO_4^{2-} complex in solution.
- When the metal is immersed in this environment, the Zn^{2+}-ATMP complex and Zn^{2+}-MoO_4^{2-} complex diffuse from the bulk of the solution to the surface of the metal.
- On the surface of the metal, the Zn^{2+}-ATMP complex is converted into Fe^{2+}-ATMP complex in the local anodic sites. Zn^{2+}-ATMP + Fe_2+ → Fe_2+-ATMP + Zn^{2+}.
- Similarly, the Zn^{2+}-MoO_4^{2-} complex is converted into iron-molybdate complex, namely, $Fe_2(MoO_4)_3$.

  $3\ Zn^{2+}$-MoO_4^{2-} + $2\ Fe^{3+}$ → $Fe_2(MoO_4)_3$ + $3\ Zn^{2+}$

  (Formation of Fe^{3+}-ATMP complex and Fe^{2+}-MoO_4^{2-} complex to some extent cannot be ruled out.)
- The released Zn^{2+} on the metal surface forms $Zn(OH)_2$ in the local cathodic regions.

  $Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2 \downarrow$
- $ZnMoO_4^{2-}$ also forms on the metal surface.

Conclusions

- The formulation consisting of 60 ppm Cl^-, 50 ppm ATMP and 300 ppm MoO_4^{2-} has 32 per cent inhibition efficiency. The inhibitive film consists of $Fe_2(MoO_4)_3$ complex.
- The formulation consisting of 60 ppm Cl^-, 50 ppm ATMP, 300 ppm MoO_4^{2-} and 50 ppm Zn^{2+} has 96 per cent inhibition efficiency. The inhibitive film consists of $Fe_2(MoO_4)_3$, $ZnMoO_4$, Fe^{2+}-ATMP complex and $Zn(OH)_2$.
- The protective film is found to be luminescent.
- This formulation may be used in cooling water systems.

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References

Breske, T.C. (1977), *Materials Perform.,* Vol. 16, p. 17.

Du Thanbao, Chen Jiajian, Cao Dianzhen and Cao Chunan (1997), *Bull.Electrochem.*, Vol.13, p. 13.

Fang, J.L., Li, Y., Ye, X.R., Wang, Z.W. and Liu, Q. (1993), *Corrosion,* Vol. 49, p. 266.

Favre, M. and Landolt, D. (1993), *Corrosion Science*, Vol. 34, p. 1481.

Galkin, T., Forsen, O., Ylasaari, S., Kotenev, V.A. and Arponen, M. (1996), EUROCORR '96, Nice, Paper No.II-R2

Gunasekaran, G., Palaniswamy, N., Apparao, B.V. and Muralidharan, V.S. (1997), *Electrochimica Acta,* Vol. 49, p. 1427.

Hatch, G.B. and Ralston, P.H. (1972), *Mat. Pro. Perf.*, Vol.11, p. 39.

Horner, L. and Horner, C.L. (1976), *Werkst. Korros.*, Vol. 27, p. 223.

Horvath, T., Kalman, E., Kutsan, G. and Rauscher, A. (1994), *British Corrosion Journal*, Vol. 29, p. 215.

Hwa, C.M. (1969), *Proc.Int.Water.Conf.*, (W.Penna, Engrs.Soc.), Vol. 30, p. 138.

Kubicki, J., Kuczkowska, S., Falewicz, P. and Pyrwanow, B. (1985), *Procedures of the 6th European Symposium on Corrosion Inhibitors*, Vol. 2, p. 1131, Ferrara, Italy.

Kuznetsov, Yu.I. and Bardasheva, T.I. (1988), *Zashch. Met.,* Vol.24, p. 234.

Rajendran, S., Apparao, B.V. and Palaniswamy N. (1996a), *Bull. Electrochem.,* Vol.12, p.15.

Rajendran, S., Apparao, B.V. and Palaniswamy N. (1996b), EUROCORR '96, 24-26 September, Nice, Paper No.II - P1.

Rajendran, S., Apparao, B.V. and Palaniswamy N. (1996c), *Procedures of the 2nd Arabian Corrosion Conference,* Kuwait, p. 483.

Rajendran, S., Apparao, B.V. and Palaniswamy, N. (1995), *Procedures of the 8th European Symposium on Corrosion Inhibitors*, Ferrara, Vol. 1, p. 465.

Sekine, I. and Kirakawa, Y. (1986), *Corrosion*, Vol. 42, p. 276.