Contributed papers

Comparison of the corrosion inhibition efficiencies of the ATMP-molybdate system and the ATMP-molybdate-Zn^{2+} system

Susai Rajendran
B.V. Apparao
V. Periasamy
G. Karthikeyan and
N. Palaniswamy

The authors

Susai Rajendran is based at the Department of Chemistry, GTN Arts College (Autonomous), Dindigul, Tamilnadu, India.

B.V. Apparao is based at the Department of Chemistry, Regional Engineering College, Warangal, Andhrapradesh, India.

V. Periasamy and **G. Karthikeyan** are based at the Department of Chemistry, Gandhigram Rural Institute, Gandhigram, India.

N. Palaniswamy is based at the Corrosion Science and Engineering Division, Central Electrochemical Research Institute, Karaikudi, Tamilnadu, India.

Abstract

The formulation consisting of 50ppm ATM and 300ppm MoO_4^{2-} had only 32 per cent efficiency in inhibiting the corrosion of mild steel immersed in a neutral aqueous environment containing 60ppm $C1^-$, whereas the ATMP (50ppm) – MoO_4^{2-} (300ppm) – Zn^{2+} (50ppm) system had 96 per cent inhibition efficiency. The lower inhibition efficiency in the former case was due to the dissolution of the protective film formed on the metal surface, and getting precipitated in the bulk of the solution; this system controlled the anodic reaction only. The latter system controlled both the anodic and cathodic reactions; the dissolution of the protective film formed on the metal surface was reduced to a greater extent.

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Several studies on the use of phosphonic acids as corrosion inhibitors have been reported in the literature[1-12]. They have been widely used as water treatment agents because of their low toxicity, high stability for hydrolysis, and high scale-resistance activity and corrosion inhibition activity in neutral aqueous media. They show synergistic effect with molybdate[6,11] and Zn^{2+}[2-7]. Our earlier work[12] revealed that the formulation consisting of 50ppm ATMP and 300ppm MoO_4^{2-} had only 32 per cent inhibition efficiency in controlling the corrosion of mild steel in a neutral aqueous environment containing 60ppm Cl^-, while the formulation consisting of 50ppm ATMP, 300ppm MoO_4^{2-} and 50ppm Zn^{2+} offered 96 per cent inhibition efficiency. The present study is undertaken to investigate the factors which have led to such a vast difference in the inhibition efficiencies, in the light of uv-visible, FTIR and luminescence spectral studies.

Experimental

Uv-visible spectra

Uv-visible absorption spectra of solutions were recorded using a Hitachi U-3400 spectrophotometer.

FTIR spectrum

FTIR spectrum was recorded in a Perkin-Elmer 1600 FTIR spectrophotometer having a resolving power of $4cm^{-1}$.

Luminescence spectra

Luminescence spectra were recorded in a Hitachi F-4500 fluorescence spectrophotometer.

Results and discussion

Analysis of uv-visible spectra

The uv-visible absorption spectra of various test solutions are given in Figure 1. The

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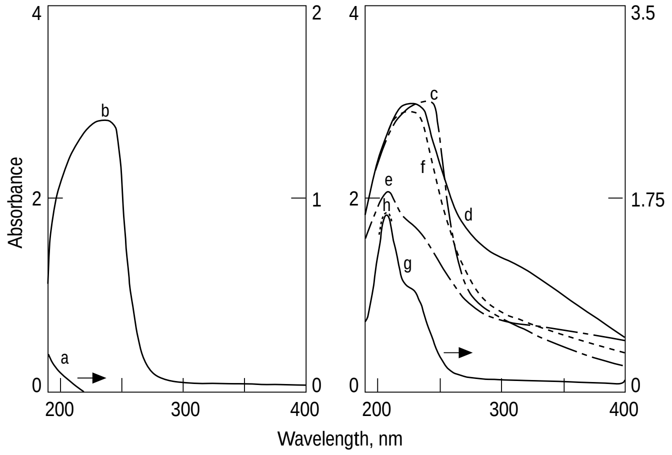
Figure 1 uv-visible absorption spectra of various test solutions: (a) ZN^{2+} 50ppm; (b) MoO_4^{2-} 300ppm; (c) MoO_4^{2-} 300ppm + Fe^{2+} 10ppm; (d) MoO_4^{2-} 300ppm + Fe^{2+} 50pm; (e) MoO_4^{2-} 300ppm + Fe^{2+} 100ppm; (f) MoO_4^{2-} 300ppm + Fe^{2+} 50ppm + Zn^{2+} 50ppm; (g) filtrate (20 times diluted) of the ATMP-MoO_4^{2-} system; (h) solution (20 times diluted) of the ATMP-MoO_4^{2-} – Zn^{2+} system



uv-visible absorption spectrum of the solution containing 50ppm Zn^{2+} is given in Figure 1a. The uv-visible spectrum of the solution containing 300ppm MoO_4^{2-} is given in Figure 1b. An identical spectrum (Figure 1b) was obtained for the solutions each containing 300ppm MoO_4^{2-} 10ppm Zn^{2+}, 300ppm MoO_4^{2-} 50ppm Zn^{2+} and also 300ppm MoO_4^{2-} 100ppm Zn^{2+}. This suggests that a loosely held Zn^{2+}-MoO_4^{2-} complex was formed in solution.

The uv-visible spectra of the diluted solutions (since the absorption was very high) of various MoO_4^{2-}-Fe^{2+} systems are given in Figure 1c,d,e. These spectra suggest the formation of Fe^{2+}-MoO_4^{2-} complex in solution.

The uv-visible absorption spectrum of the solution (diluted) containing 300ppm MoO_4^{2-}, 50ppm Zn^{2+} and 50ppm Fe^{2+} (Figure 1f) resembles that of the Fe^{2+}-MoO_4^{2-} system. This suggests that MoO_4^{2-} prefers Fe^{2+} to Zn^2 for coordination.

Comparison of ATMP-MoO_4^{2-} system and ATMP-MoO_4^{2-}-Zn^{2+} system

Our previous study[12] revealed that the formulation consisting of 60ppm Cl^-, 50ppm ATMP and 300ppm MoO_4^{2-} had only 32 per cent inhibition efficiency whereas the formulation consisting of 60ppm Cl^-, 50ppm ATMP, 300ppm MoO_4^{2-} and 50ppm Zn^{2+} had 96 per cent inhibition efficiency. To understand the reason for such a vast difference in the inhibition efficiencies, the following experiment was carried out.

Mild steel specimens were immersed in the above environments for a period of two days. Then the solutions in the beakers were subjected to the following experiments.

1. ATMP-MoO_4^{2-}-Zn^{2+} system

The solution in the beaker was very clear and colourless. Its absorption spectrum (20 times diluted) is given in Figure 1h. This spectrum resembled that of the Fe^{2+}-MoO_4^{2-} system. It suggests the presence of iron molybdate complex in solution.

2. ATMP-MoO_4^{2-}-system

The solution in the beaker was turbid and brown in colour. It was filtered. The uv-visible absorption spectrum of this solution (20 times diluted) is given in Figure 1g. It also resembled that of iron-molybdate complex. The residue was brown in colour. Its FTIR spectrum is given in Figure 2.

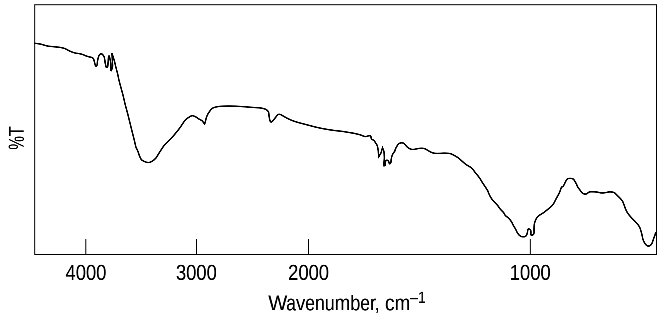
Analysis of FTIR spectrum

It is observed from Figure 2 that the P-O stretching frequency of ATMP decreased from 1,002cm^{-1} to 981.8cm^{-1}; the C-N stretching frequency decreased from 1,145cm^{-1} to 1,034cm^{-1}. It is suggested that the O atom and N atom of ATMP have coordinated with Fe^{2+} resulting in the formation of Fe^{2+}-ATMP complex[1-7,13].

It is also inferred from the spectrum that the Mo-O frequency decreased from 818.1cm^{-1} to 763.6cm^{-1}. This suggests the formation of iron-molybdate complex. Thus it is inferred that the brown residue consisted of iron-ATMP complex and iron-molybdate complex.

It is thus observed that in the ATMP-MoO_4^{2-} system (in the absence of Zn^{2+}), the iron complex formed on the anodic sites

Figure 2 FTIR spectrum of the residue of the ATMP-MoO_4^{2-} system



dissolved and went to the bulk of the solution, where it was deposited.

In the presence of Zn^{2+} (i.e. ATMP-MoO_4^{2-}-Zn^{2+} system), such precipitation was avoided, since both anodic and cathodic reactions were controlled.

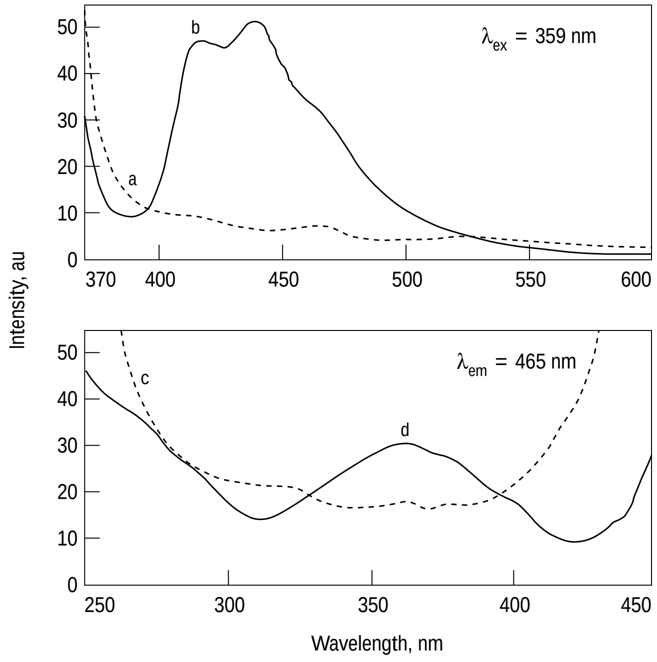
It seems from the uv-visible spectra (Figure 1g,h) that the two solutions have more or less the same intensity, suggesting that the amount of iron-molybdate complex present in the two solutions was the same. But it is expected that the amount of iron molybdate complex should be higher in the ATMP-MoO_4^{2-} system than in the ATMP-MoO_4^{2-}-Zn^{2+} system. This can be explained by the fact that a certain amount of the iron molybdate complex present in the solution became precipitated and settled at the bottom of the beaker and hence, a decrease in intensity was noticed.

Analysis of luminescence spectra

The luminescence spectra of the films formed on the surface of the metals immersed in various environments are given in Figure 3a,b,c,d.

The emission spectrum (λ_{ex} = 359nm) of the film formed on the surface of the metal immersed in the environment consisting of 60ppm Cl^-, 50ppm ATMP and 300ppm MoO_4^{2-} is given in Figure 3a. Peaks appeared at 519.4nm and 463.4nm. In the presence of Zn^{2+} (Figure 3b), a hump appeared at 465nm; peaks appeared at 416.8nm and 437.6nm. In general, a remarkable increase in intensity of the spectrum was noticed in the presence of Zn^{2+}. This suggests that the formation of iron-ATMP complex and iron-molybdate complex on the metal surface was enhanced by the presence of Zn^{2+}.

Figure 3 Luminescence spectra of the surface of the metal immersed in various environments: (a) and (c) Cl^- 60ppm + ATMP 50ppm + MoO_4^{2-} 300ppm; (b) and (d) Cl^- 60ppm + ATMP 50ppm + MoO_4^{2-} 300ppm + Zn^{2+} 50ppm



The corresponding excitation spectra (λ_{em} = 465nm) are given in Figure 3c,d. In the case of ATMP-MoO_4^{2-} system, peaks appeared at 323, 362 and 377nm; in the case of ATMP-MoO_4^{2-}-Zn^{2+} system, peaks appeared at 362 and 377nm. An increase in intensities of the peaks was noticed in the presence of Zn^{2+}. This confirms the enhanced formation of the protective film in the presence of Zn^{2+}.

Thus, analysis of luminescence spectra confirms that the formation of the protective film on the metal surface was enhanced in the presence of Zn^{2+}. This accounts for the higher inhibition efficiency of the ATMP-MoO_4^{2-}-Zn^{2+} system.

Conclusions

The ATMP (50ppm)-MoO_4^{2-} (300 ppm) system had only 32 per cent inhibition efficiency. The lower inhibition efficiency of this system was due to the dissolution of the protective film formed on the surface of the metal, going to the bulk of the solution and becoming precipitated. This system controlled the anodic reaction only.

The ATMP (50ppm)-MoO_4^{2-} (300 ppm)-Zn^{2+} (50 ppm) system had 96 per cent inhibition efficiency. This system controlled anodic and cathodic reactions. The dissolution of the protective film formed on the metal surface was reduced to a greater extent. This accounts for the higher inhibition efficiency of the system.

References

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

2 Gunasekaran, G., Palaniswamy, N., Apparao, B.V. and Muralidharan, V.S., *Electrochim. Acta*, Vol. 49, 1997, p. 1427.

3 Rajendran, S., Apparao, B.V. and Palaniswamy, N., *Proc. 8th Europ. Symp. Corros. Inhibitors*, Ferrara, Italy, Vol. 1, 1995, p. 465.

4 Rajendran, S., Apparao, B.V. and Palaniswamy, N., *EUROCORR '96*, 24-26 September 1996, Nice, France, Paper No. II – p. 1.

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

6 Rajendran, S., Apparao, B.V. and Palaniswamy, N., *Proc. 2nd Arabian Corrosion Conference*, Kuwait, 1996, p. 483.

7 Rajendran, S., Apparao, B.V. and Palaniswamy, N., EUROCORR '97, The European Corrosion Congress, Trondheim, Norway, 22-25 September 1997.

8 Veres, A., Reinhard, G. and Kalman, *E., Br. Corros. J.*, Vol. 27, 1992, p. 147.

9 Kalman, E., Varhegyi, B., Bako, I., Felhosi, I., Karman, F.H. and Shaban, A., *J. Electrochem. Soc.*, Vol. 141, 1994, p. 3357.

10 Shaban, A., Kalman, E. and Biczo, I., *Corros. Sci.*, Vol. 35, 1993, p. 1463.

11 Airey, K., Armstrong, R.D. and Handyside, T., *Corros. Sci.*, Vol. 28, 1988, p. 449.

12 Rajendran, S., Apparao, B.V., Mani, A. and Palaniswamy, N., *Anti-Corros. Methods and Materials*, January/February 1998.

13 Horner, L. and Horner, C.L., *Werkst. Korros.*, Vol. 327, 1976, p. 223.