Synergistic and Antagonistic Effects of Sodium Molybdate-Zn²⁺ System

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Received 18 August 2011; Revised 5 November 2011; Accepted 9 November 2011

Abstract: The inhibition efficiency(IE) of sodium molybdate (SM) in controlling corrosion of carbon steel in an aqueous solution containing 120 ppm of Cl⁻ in the absence and presence of Zn²⁺ has been evaluated by weight-loss method. A synergistic effect exists between SM and Zn²⁺ when the concentration of Zn²⁺ is 25 ppm and above. Inhibition efficiencies obtained are greater than 85%. Antagonistic effect exists between SM and Zn²⁺ when the concentration of Zn²⁺ is 10 ppm and below. The SM- Zn²⁺ system shows excellent IE up to third day. Above third day IE decreases. Acceleration of corrosion takes place. Excellent IE is shown at pH 5,7 and 12. At pH 9, IE decreases since Zn²⁺ is precipitated as Zn(OH)₂ in the bulk of the solution. Polarization study reveals that SM- Zn²⁺ system functions as a mixed inhibitor. FTIR spectra reveal that the protective film consists of Fe²⁺-SM complex and Zn(OH)₂.

Keywords: Carbon steel, Corrosion inhibition, Sodium molybdate, Synergistic effect, Antagonistic effect.

Introduction

Sodium molybdate is an effective corrosion inhibitor even at very low concentration. It is environmentally safe and nontoxic. It is effective over a wide pH range. Molybdate – based corrosion inhibitor systems for cooling water system has been commercially applied for many

years. Due to increasing environmental constraints on the use of chromate treatment, molybdate represents a logical, environmentally acceptable alternative. Other "Chrome alternative" like inorganic phosphate, zinc and all organic treatment have been far more popular. The application of sodium molybdate as a corrosion inhibitor in open recirculation system and closed looped cooling and heating system is increasing. The two driving forces for these increased applications are the low toxicity of the material and the fact that molybdenum is thought to have similar chemistry to that of chromium. Molybdate, a new formulation, recently made available, takes advantage of molybdate's anodic film – forming properties. Molybdate anion has been widely used as corrosion inhibitor since 1939 because of its efficiency towards both ferrous and nonferrous metal and its way low order of toxicity. Molybdate has been used as inhibitor in combination with nitrite¹⁻³, alkyl amine phosphate^{4,6} and azoles like benzotriazole and polytriazole⁷. The inhibition effects of molybdate and tungstate on the corrosion of cold rolling steel (CRS) in hydrochloric acid solution (0.1–0.5 M) were investigated by weight loss and electrochemistry methods⁸. The corrosion inhibition of molybdate- nitrite anions on mild steel⁹ & oxyanions of tungstate - molybdate on 304 stainless steel have been investigated¹⁰. Chen *et al.* found the effect of denitrifying Fe-oxidizing bacteria TPH -7 on corrosion inhibition of sodium molybdate¹¹. Molybdate has high corrosion resistance and high coating performance on steel¹²⁻¹⁴, galvanized steel^{15,16} and aluminium alloys^{17,18}. The synergistic effect of molybdate – Zn²⁺ system¹⁹⁻²³ and inhibition efficiency²⁴⁻²⁶ have been investigated. Even though several studies have been reported on the synergistic effect of molybdate –Zinc system the mechanistic aspects have not been studied in detail. The present work is undertaken (i) to evaluate the inhibition efficiency of sodium molybdate (SM) in controlling corrosion of carbon steel in aqueous solution containing 120 ppm of Cl⁻ in the absence and presence of Zn²⁺ (ii) to study the synergistic and antagonistic effect of the SM-Zn²⁺ system (iii) to analyze the protective film by FTIR (iv) to study the mechanistic aspects of corrosion inhibition by polarization study and (v) to propose a suitable mechanism of corrosion inhibition based on the results from the above studies.

Experimental

Carbon steel specimens (0.026%S, 0.06%P, 0.4%Mn, 0.1%C and the rest Iron) of the dimensions 1.0x4.0x0.2cm were polished to a mirror finish and degreased with trichloroethylene, and used for the weight-loss method and surface examination studies.

Weight-loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn²⁺ for one day. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. The corrosion products were cleansed with Clarke's solution²⁷. The corrosion inhibition efficiency (IE) was then calculated using the equation

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

where, w_1 = corrosion rate in absence of inhibitor, w_2 = corrosion rate in presence of inhibitor.

Potentiostatic polarization study

This study was carried out using EG & G electrochemical impedance analyzer model 6310. A three-electrode cell assembly was used. Carbon steel was used as working electrode, platinum was used as counter electrode and saturated calomel electrode (SCE) was used as reference electrode. Corrosion potential, corrosion current and Tafel slopes were calculated.

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by various surface analysis techniques.

FTIR spectra

These spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets and the FTIR spectra were recorded.

Results and Discussion*Weight-loss study*

Corrosion rates of carbon steel in aqueous solution containing 120 ppm of Cl^- in the absence and presence of inhibitor at various concentrations have been measured by weight-loss study. The corrosion inhibition efficiencies of sodium molybdate (SM) are also given in Table 1. It is found that SM shows some IE. As the concentration of SM increases, IE also increases.

Table 1. Corrosion rates(CR) of Carbon steel in aqueous solution in the presence of inhibitor and the inhibition efficiency obtained by weight loss method. Inhibitor System: $\text{SM} + \text{Zn}^{2+}$ pH=7, Immersion Period: one day.

Cl^- ppm	SM ppm	Zn^{2+} ppm	CR mdd	IE %
120	0	0	20.00	-
120	50	0	16.00	20
120	100	0	14.00	30
120	150	0	13.00	35
120	200	0	11.00	45
120	250	0	9.00	55

Influence of Zn^{2+} on the IE of SM

The influence of Zn^{2+} on the IE of SM is given in Table 2. It is found that as the concentration of Zn^{2+} increases, IE of SM increases. Similarly, for a given concentration of Zn^{2+} , as the concentration of SM increases, IE also increases. A synergistic effect exists between SM and Zn^{2+} . For example 50 ppm of SM and only 20% IE. However their combination has 96% IE. This confirms that this formulation has a synergistic effect. This can be explained by the fact that in the presence of the anodic reaction $[\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-]$ is controlled by the formation of iron molybdate complex on the anodic sites of the metal surface. In the presence of Zn^{2+} , the anodic reaction is controlled by the formation of iron molybdate complex on the anodic sites of the metal surface; and the cathodic reaction $[2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \longrightarrow 4\text{OH}^-]$ is controlled by the formation of $\text{Zn}(\text{OH})_2$ on the cathodic sites of the metal surface. It is to be noted that synergistic is noticed only when the concentration of Zn^{2+} is 25 ppm and above. At 5 ppm and 10 ppm Zn^{2+} synergistic effect is not noticed, but an antagonistic effect is noticed. At low concentration of Zn^{2+} , the amount of SM transported towards the metal surface from the bulk of the solution is less; the amount of SM surrounding the Zn^{2+} ion is high in the bulk of the solution. Hence an antagonistic effect, namely, a decrease in IE is noticed.

Table 2. Inhibition Efficiency(%) of various SM-Zn²⁺ system, when carbon steel is immersed in aqueous solution for one day. Cl⁻ =120 ppm pH=7.

SM ppm	Zn ²⁺ , ppm					
	0	5	10	15	50	
0	-	Acceleration of Corrosion				
50	20	10	15	85	96	
100	30	15	25	92	96	
150	35	20	30	94	97	
200	45	25	40	95	98	
250	55	35	45	97	98	

Influence of immersion period on IE

The influence of immersion period on IE of SM-Zn²⁺ system is given in Table 3. Very good IE is shown up to third day. After wards the IE decreases. The protective film is broken by the aggressive chloride ion present in the medium²⁸.

Table 3. Influence of immersion period on the IE, Cl⁻ = 120 ppm SM = 50 ppm, Zn²⁺ = 50 ppm pH = 7.

Day	1	3	5	7
IE (%)	96	96	Acceleration of Corrosion	

Influence of pH on the IE

The influence of pH on the IE of the SM- Zn²⁺ is given in Table 4. It is found that at pH 5 and 7, good IE is shown by the inhibitor system. At pH 9 the IE decreases from 96% to 64%. This is due to the fact that when pH is changed to 9 by addition of NaOH, Zn²⁺ is precipitated as Zn(OH)₂ in the bulk of the solution. Hence SM is not transported to the metal surface by Zn²⁺ effectively. The amount of SM on the metal surface is less. Hence the amount of protective film (iron molybdate complex) formed on the metal surface is less.

Table 4. Influence of pH on the IE, Cl⁻ = 120 ppm, SM = 50 ppm, Zn²⁺ = 0 ppm, Immersion period = one day.

pH	5	7	9	12
IE, %	98	96	64	92

So the IE decreases. However at high pH value namely, 12, the IE again increases. This is due to the fact at higher pH value of 12, (addition of more NaOH), insoluble Zn(OH)₂ is converted in to soluble sodium zincate and zinc ions are ready to transport more SM towards the metal surface. So IE increases as the protective film is strengthened by the formation of more iron molybdate complex.

Analysis of potentiostatic polarization curves

The potentiostatic polarization curves of carbon steel in the aqueous solution containing Cl⁻ and inhibitors are shown in Figure 1. The corrosion parameters are given in Table 5. When carbon steel is immersed in chloride environment, the corrosion potential is -386 mV vs saturated calomel electrode(SCE). The formulation consisting of 50 ppm of SM and 50 ppm

of Zn^{2+} has corrosion potential of -380mV vs SCE. It is not shifted very much. The Tafel slopes b_a and b_c for this system are almost equal (108 mV/decade and 110 mV/decade). These results suggest that the formulations consisting of Cl^- , SM and Zn^{2+} function as a mixed inhibitor, controlling the anodic reaction of formation Fe^{2+} and cathodic reaction of formation of OH^- , to the same extent.

Analysis of FTIR spectra

FTIR spectrum (KBr) of pure sodium molybdate (SM) is shown in Figure 2a. The Mo-O stretching frequency appears at 829 cm^{-1} . The FTIR spectrum(KBr) of film formed on the surface of metal after immersion in the solution containing Cl^- , SM and Zn^{2+} for one day, was carefully removed, mixed with KBr thoroughly and made in pellet form. The FTIR spectrum of this film is shown in Figure 2b. The Mo-O stretching frequency has decreased from 829 m^{-1} to 825 cm^{-1} . This indicates that oxygen atom of SM has coordinated with Fe^{2+} on the metal surface^{29,30}. The peak at 1350 cm^{-1} is due to $\text{Zn}(\text{OH})_2$ formed on the cathodic sites³¹. Thus FTIR spectra lead to the conclusion that the protective film consists of iron molybdate and $\text{Zn}(\text{OH})_2$.

Figure 1. Polarization curves of carbon steel immersed in various test solution, (a) Cl^- 120 ppm, (b) Cl^- 120 ppm + SM 50 ppm + Zn^{2+} 50 ppm.

Figure 2. FTIR Spectra (KBr), (a) Pure sodium molybdate (SM), Film formed on carbon steel after immersion in solution containing 120 ppm of Cl^- + 50 ppm of SM + 50 ppm of Zn^{2+} .

Table 5. Corrosion parameters of carbon steel immersed in various test solution obtained by polarization method, $\text{pH}=7$.

Cl^-	SM ppm	Zn^{2+} ppm	E_{corr} mV vs SCE	b_a mV	b_c mV
120	0	0	-386	112	96
120	50	50	-380	108	110

Mechanism of corrosion inhibitor

The results of the weight-loss study show that the formulation consisting of 50 ppm SM and 50 ppm Zn^{2+} has 96% IE. Polarization study reveals that this formulation functions as a mixed inhibitor. FTIR spectral study reveals that the protective film consists of iron

molybdate complex and Zn(OH)_2 . In order to explain these facts the following mechanism of corrosion inhibition is proposed.

- When the solution consisting of 120 ppm Cl^- , 50 ppm of Zn^{2+} is prepared, there is formation of $\text{Zn}^{2+}\text{-MoO}_4^{2-}$ complex in solution.
- When carbon steel is immersed in this solution, the $\text{Zn}^{2+}\text{-MoO}_4^{2-}$ complex diffuses from the bulk of the solution towards metal surface.
- On the metal surface, $\text{Zn}^{2+}\text{-MoO}_4^{2-}$ complex is converted into iron molybdate complex on the anodic sites. Zn^{2+} is released.

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

Conclusion

The present study leads to the following conclusions:

- ❖ The inhibition efficiency (IE) of sodium molybdate (SM) in controlling corrosion of carbon steel in an aqueous solution containing 120 ppm of Cl^- in the absence and presence of Zn^{2+} has been evaluated by weight-loss method.
- ❖ A synergistic effect exists between SM and Zn^{2+} when the concentration of Zn^{2+} is 25 ppm and above. Inhibition efficiencies obtained are greater than 85%.
- ❖ Antagonistic effect exists between SM and Zn^{2+} when the concentration of Zn^{2+} is 10 ppm and below.
- ❖ The SM- Zn^{2+} system shows excellent IE up to third day. Above third day IE decreases. Acceleration of corrosion takes place.
- ❖ Excellent IE is shown at pH 5, 7 and 12. At pH 9, IE decreases since Zn^{2+} is precipitated as Zn(OH)_2 in the bulk of the solution.
- ❖ Polarization study reveals that SM- Zn^{2+} system functions as a mixed inhibitor.
- ❖ FTIR spectra reveal that the protective film consists of Fe^{2+} -SM complex and Zn(OH)_2 .

Acknowledgment

The authors are thankful to their respective managements, Prof. Susai Rajendran is thankful to UGC for help and encouragement.

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