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Corrosion inhibition of mild steel by organic inhibitor in well water environment

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ABSTRACT

The corrosion inhibition efficiency (IE) of 1, 1'Carbonyldiimidazole (CDI) in controlling the corrosion of mild steel immersed in well water for one day in the presence and absence of Zn^{2+} has been studied by mass loss method. The formulation consisting of 100 ppm of CDI and 100 ppm Zn^{2+} offers 72% inhibition efficiency. The synergistic effect exists between CDI and Zn^{2+} system. The additive sodium gluconate (SG) was added with best formulation to enhance the IE. The addition of 100 ppm of SG increased the IE from 72% to 93%. Polarization study shows that the best formulation system controls anodic reaction predominantly. The FTIR spectra study leads to the conclusion that the Fe^{2+}-CDI and Fe^{2+}-SG complex formed on anodic sites of the metal surface controlling the anodic reaction and $Zn(OH)_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction. The mechanism of corrosion inhibition is proposed based on the results obtained from mass loss study, polarization study FTIR study.

Key Words: Mild steel, 1, 1'carbonyldiimidazole (CDI), Inhibition efficiency, protective film.

INTRODUCTION

Corrosion is the deterioration of a metal by chemical or electrochemical reaction with its environment.The corrosion of metals in many industries, constructions, installations, and civil services such as electricity, water, and sewage supplies is a serious problem. The Cooling systems are exposed to many types of corrosion from general electrochemical corrosion, to pitting caused by deposits, electrolysis, or microorganisms. Corrosion can reduce the life-span of equipment by years, requiring expensive replacement. It can lead to costly equipment repairs and production downtime. Corrosion related deposits lead to reduced capacity and wasted energy because of heat transfer efficiency losses. In order to prevent or minimize corrosion, the corrosion inhibitors are usually used in flow cooling water systems. The organic compounds and several carboxylates such as sodium salicylate, sodium cinnamate and adipate have been used as inhibitors. Synergistic effect of succinic acid and Zn^{2+} in controlling corrosion of carbon steel in well water has been reported. The inhibitor 1,1'Carbonyl diimidazole (CDI) is chosen as the corrosion inhibitor for this present work. The literature presents some studies involving imidazole having the ability to prevent the corrosion of iron.

The aim of the present study is

1. To evaluate the inhibition efficiency of 1, 1'carbonyl diimidazole in controlling the corrosion of mild steel in the absence and presence of Zn^{2+}.

2. To enhance the inhibition efficiency of CDI, the additive sodium gloconate are added.

3. To study the mechanistic aspects by potentio dynamic polarization study.

4. To analyze the protective film on carbon steel by FTIR spectrophotometer.

5. To propose a suitable mechanism for corrosion inhibition based on the results from the above study.

MATERIALS AND METHODS

Preparation of the specimen: Mild steel (0.026%S, 0.06%P, 0.4%Mn, 0.1% C, and the rest Fe) specimen of dimension 1 cm x 4 cm x 0.2 cm were used for weight loss study. Mild steel specimens were polished to a mirror finish with help emery paper of different grade and degreased with trichloroethylene.

Weight loss method: The well water used in this study are given in Table 1. Mild steel specimens in triplicate were immersed in 100 ml of well water containing various concentrations of the inhibitors, in the absence and presence of and Zn^{2+} ions, for a period of one day.

Table.1.

Parameters	Value
pH	8.5
Conductivity	3100 μmhos/cm
TDS	2010 ppm
Chloride	590 ppm
Sulphate	14 ppm
Total Hardness	1100 ppm

The weight of the specimens before and after immersion was determined using Shimadzu balance, AY62 model. The corrosion products were cleansed with Clarke's solution. The corrosion rates (CR) of the metal specimens were calculated with the help of the following relationship:

$$CR = \frac{\Delta m}{A * t} \qquad (1)$$

where
CR - corrosion rate
Δm - loss in weight (mg)
A - surface area of the specimen (dm^2)
t - Period of immersion (days)
The inhibition efficiency (*IE*) was then calculated using the equation

$$IE = 100\left(1 - \frac{W_2}{W_1}\right) \qquad (2)$$

Where, W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

Polarization study: Polarization studies were carried out by using CHI electrochemical impedance analyzer, model 660 A.. A three electrode cell assembly was employed. The working electrode used was rectangular mild steel with one face of the electrode exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. According to the stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current

$$I_{corr} = b_a \times b_c / \ 2.303\ (b_a + b_c)\ R_p$$

Where, R_p is polarization resistance.

The results, such as Tafel slopes (b_a and b_c), and corrosion current (I_{corr}) and corrosion potential (E_{corr}) values were calculated.

Surface analysis by FTIR spectra: The metal specimens were taken out of from the test solutions, washed and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so was to make it uniform throughout. FTIR spectrum of the powder (KBr pellet) was recorded using Perkin – Elmer 1600 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Analysis of results of mass loss method: The corrosion inhibition efficiency of mild steel immersed in well water in the absence and presence of inhibitor systems are given in Table 2 to Table 4. It is seen from Table 1 that the CDI alone is poor inhibitor. But in presence of Zn^{2+}, it shows some IE. As concentration CDI increases, IE increases. For example 400 ppm of CDI alone shows **10**% IE; But addition of 100 ppm of Zn^{2+} with CDI shows 72% IE. This suggests that a synergistic effect exists between CDI – Zn^{2+} system.

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Table 2. Corrosion inhibition efficiency (IE) of mild steels in well water in the presence of inhibitor obtained by mass loss method

Inhibitor system: CDI alone
Period of immersion: one day

CDIppm	Zn^{2+}(ppm)	IE%
0	-	-
50	0	-5
100	0	3
200	0	5
300	0	8
400	0	10
500	0	11

Table 3. Corrosion inhibition efficiency (IE) of mild steels in well water in the presence of inhibitor obtained by mass loss method.

Inhibitor system: Zn^{2+} system.
Period of immersion: one day

CDI ppm	Zn^{2+} (ppm)	IE %
0	-	-
0	10	2
0	50	3
0	100	8
0	150	12
0	200	15
0	250	18

Table 4. Corrosion inhibition efficiency (IE) of mild steels in well water in the presence of inhibitor obtained by weight loss method.

Inhibitor system: CDI –Zn^{2+} system
Period of immersion: one day

CDIppm	Zn^{2+}(ppm)	IE%
0	-	-
50	100	43
100	100	52
200	100	65
300	100	68
400	100	72
500	100	72

Influence of sodium gluconate on the inhibition efficiency with Zn^{2+} system: The influence of sodium gluconate(SG) on the inhibition efficiency with CDI - Zn^{2+} system is given Table 5. When various concentration of SG added to the CDI –Zn^{2+} system, the inhibition efficiency does not altered. The Zn^{2+} - CDI and Zn^{2+} - SG systems are much transported towards the metal surface, hence protective film is stable.

Table 5. Corrosion inhibition efficiency (IE) of mild steels in well water in the presence of inhibitor obtained by weight loss method.

Inhibitor system: CDI –Zn^{2+} -SG system

Period of immersion: one day

CDI ppm	Zn^{2+} (ppm)	SG ppm	IE %
0	-		-
400	100	50	89
400	100	100	93
400	100	200	93
400	100	300	93
400	100	400	93
400	100	500	93

Analysis of polarization study: The polarization curves of mild steel immersed in well water in the presence and absence of inhibitors are shown in Figure 2. The corrosion parameters are given in Table 6.

When the mild steel immerse in well water, the corrosion potential (E_{corr}) is -485 mV Vs SCE. The formulation consisting of 400 ppm of CDI, 100ppm of Zn^{2+} and 100 ppm of SG shifts the corrosion potential from -485 to -507 mV Vs SCE. That is corrosion potential shifts to cathodic direction (from -485 mV to -507 mV). This suggests that the cathodic reaction is controlled predominantly.

Table.6.Corrosionparametersofcarbonsteel immersed in varioustestsolutionobtained bypolarization method.

Description	E_{corr} mV/decade	b_a mV/decade	b_c mV/decade	I_{corr} A/cm^2
Well water	-485	479	541	1.133×10^{-6}
400 ppm of CDI , 100 ppm of Zn^{2+} and 100 ppm of SG	-507	610	517	2.910×10^{-5}

Now the shifts in the anodic and cathodic slopes can be compared. Tafel values for the well water are different. The Tafel values for the formulation are not equal (ba = 610 mV/decade b_c = 517 mV/decade)

When the mild steel immerse in well water, the corrosion current (I_{corr}) is 1.133×10^{-6} A/cm^2. It is decreased to 2.910×10^{-5}A/cm^2 for the best formulation. The current of the iron dissolution is decreased significantly indicating that the metal surface was passivated by the formed inhibitor layer. The passivity ion is probably due to the formation of CDI – Fe^{2+} surface layer.

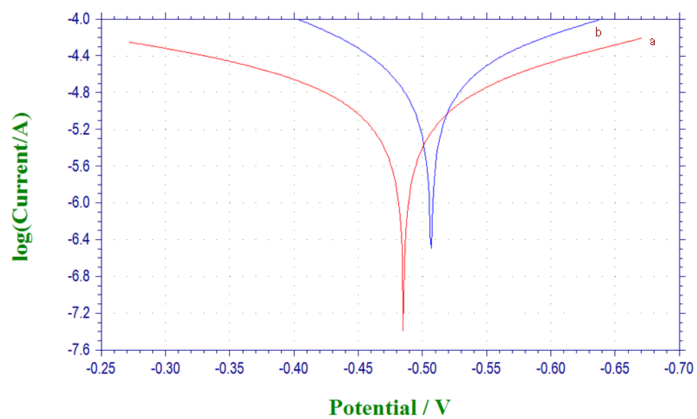

Figure 2: Polarization curves of carbon steel immersed in various test solution

a. Well water

b. Well water contains 400 ppm of CDI, 100 ppm Zn^{2+} and 100 ppm SG

The significant reduction in corrosion current for inhibitor formulation may indicate more adsorption of the inhibitors and better inhibitions performance. This result suggests that a protective film is formed on the metal surface. This protects the metal from corrosion.

Analysis of FTIR spectra: The FTIR spectrum of pure 1, 1'carbonyldiimidazole is shown in Figure 2a. The C=O stretching frequency of carbonyl group appears at 1668 cm-1. The C-N and N-H stretching frequency appears at 1142 cm-1 and 3118 cm-1respectively. The FTIR spectrum (KBr pellet) steel surface after immersion in the well water containing 400 ppm of CDI, 100 ppm Zn^{2+} and 100 ppm of SG system is shown in Figure 2b. The C=O stretching frequency has decreased from 1668 cm-1 to 1576 cm-1. The C-N stretching frequency has decreased from 1142 cm-1 to 1109 cm-1. The N-H stretching frequency has shifted from 3118 cm-1 to 3396 cm^{-1}.

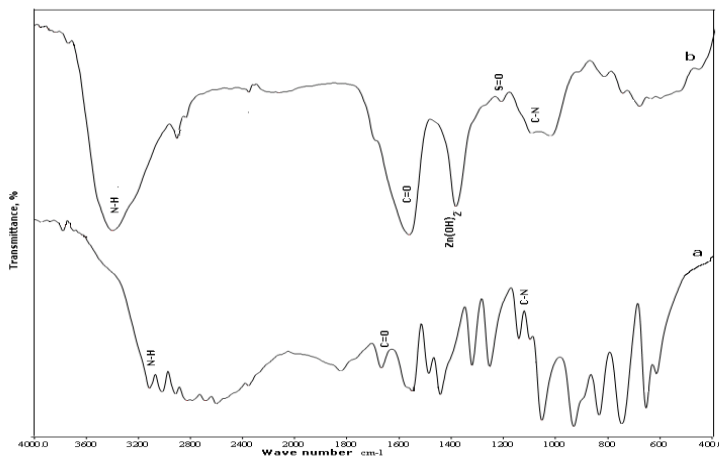

Figure.2.Analysis of FTIR spectra

a. **Pure 1,1' carbonyldiimidazole**
b. **Film formed on mild steel after immersion in well water containing 400 ppm of CDI, 100 ppm of Zn^{2+} and 100 ppm of SG**

This indicates that these groups of CDI has coordinated Fe^{2+} , resulting the formation of Fe^{2+} - CDI complex on anodic sites of metal surface. It is found that the S=O stretching frequency appears at 1224 cm^{-1}. The SG has coordinated with Fe^{2+} resulting the formation of Fe^{2+} - SG complex also formed on the anodic sites of metal surface. The peak at 1398 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface. Thus FTIR spectra study leads to the conclusion that the Fe^{2+} - CDI and Fe^{2+} - SG complexes formed on anodic sites of the metal surface controlled the anodic reaction and $Zn(OH)_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction[9,10].

Mechanism of corrosion inhibition: The mass – loss study reveals that the formulation consisting of 100 ppm of Zn^{2+}, 400 ppm of CDI and 100 ppm of SG has 93 % inhibition efficiency. A mechanism of corrosion inhibition proposed based on mass loss method, polarization studies and FTIR spectral studies.

In order to explain the above observations, the following mechanism of corrosion inhibition is proposed.

- When the environment consisting of 100 ppm of Zn^{2+}, 400 ppm of CDI and 100 ppm of SG are prepared, there is a formation of Zn^{2+} -CDI complex and Zn^{2+} - SG complex in solution.
- When the mild steel is introduced in this solution, there is diffusion of Zinc complexes move towards the metal surface.
- On the metal surface Zinc complex is converted into iron complex on the anodic site.

$$Zn^{2+}\text{-CDI} + Fe^{2+} \rightarrow Fe^{2+}\text{- CDI} + Zn^{2+}$$
$$Zn^{2+}\text{-SG} + Fe^{2+} \rightarrow Fe^{2+}\text{- SG} + Zn^{2+}$$

- The released Zn^{2+} combined with OH^- to form $Zn(OH)_2$ on the cathodic Sites.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$$

- Thus, protective film consists of Fe^{2+} - CDI complex, Fe^{2+}- SG complex and $Zn(OH)_2$. The mechanism of corrosion inhibition is shown in figure 3.

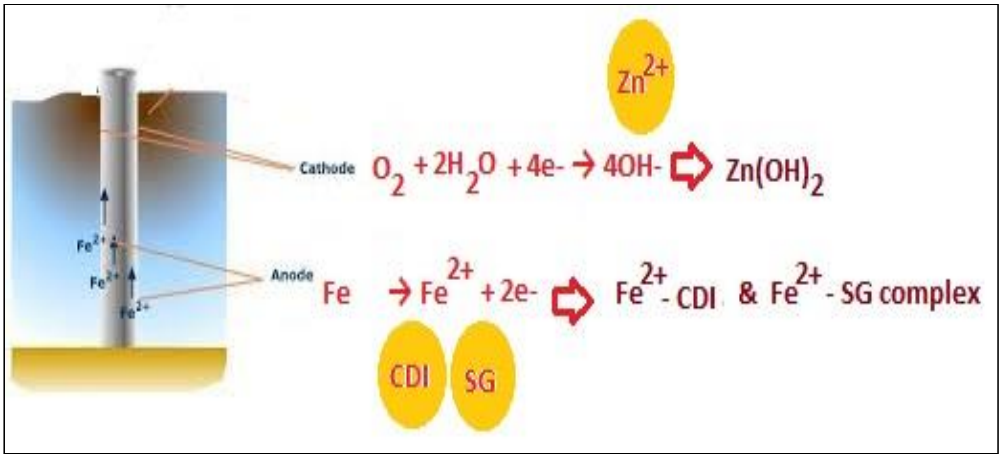

Figure.3.Mechanism of Corrosion Inhibition

CONCLUSION

The present study leads to the following conclusions:

- ✓ The formulation consisting of 100 ppm of Zn^{2+}, 400 ppm of CDI and 100 ppm of SG offers 93% inhibition efficiency;
- ✓ The synergistic effect exists between CDI – Zn^{2+}- SG system. The mixed inhibitors show better inhibition efficiency than individual.
- ✓ Polarization study reveals that this formulation controls the anodic reaction predominantly;
- ✓ FTIR spectra reveal that the protective film consists of Fe^{2+} - CDI complex and Fe^{2+}- SG complex formed on anodic sites of metal surface and $Zn(OH)_2$ formed on cathodic sites of metal surface.

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