Methyl orange as corrosion inhibitor for carbon steel in well water

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The corrosion inhibition efficiency of methyl orange in controlling corrosion of carbon steel immersed in well water has been evaluated by weight loss method both in absence and presence of zinc ion. A synergistic effect exists between methyl orange (MO) and Zn^{2+}. The inhibition efficiency (IE) of the MO – Zn^{2+} system decreases with increase in immersion period. Polarization study suggests that the MO-Zn^{2+} system functions as a mixed inhibitor system. FTIR spectra indicate that the protective film consists of Fe^{2+} - MO complex and $Zn(OH)_2$.

Keywords: Carbon steel, Corrosion inhibition, Methyl orange, Zinc ion

Several compounds such as nitrite[1,2], phosphates[3,4], silicates[5], sodium salicylate[6], sodium cinnamate[7], molybdate[8,9], phosphonic acids[10,11], polyacrylamide[13] and caffeine[14,15] have been used as corrosion inhibitors. Talati and Gandhi[16-18] have studied the effect of some dyes as corrosion inhibitors for B26S aluminium in hydrochloric acid. The inhibition efficiency (IE) of triphenylmethane dyes such as victoria blue, fast green, light green, malachite green, fuchsine base, fuchsine acid, crystal violet and methyl violet 6B in controlling corrosion of aluminium in phosphoric acid has been studied by Talati and Daraji[19] using weight loss and polarization studies. Corrosion inhibition of mild steel in acidic media by some organic dyes have been investigated[20]. Oguzie[21] has studied the inhibition of corrosion of mild steel in hydrochloric acid solution by methylene blue dye. Eriochrome Black-T serves as a good corrosion inhibitor for carbon steel in well water[22]. At *p*H 11 methyl orange along with Zn^{2+} functions as a good inhibitor in controlling corrosion of aluminium[23]. Dyes have chromophores and auxochromes. They can form films on metal surfaces by coordination through azo groups and/or π electrons of aromatic rings. Though several dyes have been used as corrosion inhibitors, the mechanistic aspects of corrosion inhibition have not been studied in detail. Present study was aimed to investigate (i) the inhibition efficiency of methyl orange (MO) in controlling the corrosion of carbon steel immersed in well water in the absence and presence of zinc ion, (ii) the influence of *p*H and immersion period (iii) to analyze the protective film formed on the metal surface by FTIR spectroscopy (iv) to propose a suitable mechanism of corrosion inhibition based on the results of electrochemical study such as polarization and FTIR spectra.

Experimental Procedure

Preparation of specimens

Carbon steel specimens (S, 0.0267; P, 0.067; Mn, 0.4; C, 0.1% and the rest iron), of the dimensions 1.0×4.0×0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for weight loss method and surface examination studies.

Weight loss method

Relevant data of the well water used in this study are given in Table 1. Carbon steel specimens, in triplicate, were immersed in 100 mL of the well water and various concentrations of methyl orange in the presence and absence of Zn^{2+} (as $ZnSO_4.7H_2O$) for a period of one day. The corrosion products were cleaned with Clarke's solution[24]. The weight of the specimens before and after immersion was determined using Shimadzu balance AY62. The corrosion inhibition efficiency was calculated using Eq. (1)

$$IE = 100 \left(1 - W_2 / W_1\right) \% \qquad \qquad \text{.... (1)}$$

where W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in presence of inhibitor.

FTIR spectra

The structure of methyl orange is shown in Fig. 1. The carbon steel specimens immersed in various test solutions for one day were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin–Elmer–1600 spectrophotometer.

Potentio dynamic polarization study

Polarization study was carried out in electrochemical impedance analyzer model CHI 660A, using a three electrode cell assembly; *iR* compensation was made. Carbon steel was used as working electrode with platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic slope, b_a and cathodic slope, b_c) were calculated.

Results and Discussion
Weight loss study

The corrosion inhibition efficiencies (IE) of methyl orange in controlling the corrosion of carbon steel immersed in well water, both in the absence and presence of zinc ion have been tabulated in Table 2. The values indicate that the ability of methyl orange

as a good corrosion inhibitor is enhanced significantly in presence of Zn^{2+}.

Influence of immersion period on inhibition efficiency

The IE of 100 ppm MO-50 ppm Zn^{2+} system (Table 3) is found to decrease as the immersion period increases. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as Cl^- ion (665 ppm) present in well water. There is a competition between the formations of $FeCl_2$ (and also $FeCl_3$) and Fe–MO complex (on the anodic sites of the metal surface). A perusal of the results suggests that the formation of $FeCl_2$ is favoured when compared with the formation of Fe-MO complex[25,26]. Similar observations have been made by Selvaraj *et al.*[25], while studying corrosion inhibition, using polyvinyl pyrrolidone and also by Rajendran *et al.*[26], while investigating corrosion inhibition by sodium dodecyl sulphate.

Influence of *p*H on inhibition efficiency

The IE of the MO–Zn^{2+} system has been evaluated at different *p*H values of the solutions. IE values have been tabulated in Table 4. At *p*H 6 the IE is found to be 64%. This decrease in IE is due to the fact that the protective film formed on the metal surface is broken by the attack of H^+ ions. At *p*H 8 the IE is 98%. Further increase in *p*H of the solution lowers IE substantially. Experimental results suggest that the amount of Zn^{2+} available to transport MO towards the metal surface decreases at high *p*H. This may be due
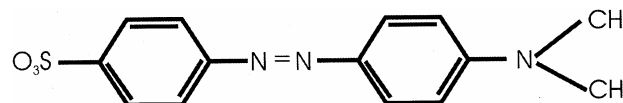
Table 1—Parameters of well water

Parameter	Value
*p*H	8.38
Conductivity	3110 μmhos / cm
TDS	2013 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

Fig. 1—Structure of methyl orange

Table 2—Corrosion rates (CR) of carbon steel in well water in the absence and presence of inhibitor and the inhibition efficiencies obtained by weight loss method.

Inhibitor system : Methyl orange (MO) + Zn^{2+} Immersion period : One day

MO (ppm)	Zn^{2+} = 0 (ppm)		Zn^{2+} = 10 (ppm)		Zn^{2+} = 25 (ppm)		Zn^{2+} = 50 (ppm)	
	CR (mdd)	IE (%)	CR (mdd)	IE (%)	CR (mdd)	IE (%)	CR (mdd)	IE (%)
0	59.09	--	56.14	5	50.23	15	46.09	22
20	78.17	-32	1.185	96	10.05	83	4.14	93
60	69.08	-17	1.174	98	9.45	84	2.95	95
100	58.19	2	1.168	98	5.32	91	1.183	98
140	55.46	6	1.159	98	4.73	92	1.182	98
180	51.82	12	1.153	98	2.36	96	1.181	98

Table 3—Influence of immersion period on the inhibition efficiency of the MO – Zn^{2+} system

Immersion period (day)	System		
	Well water	Well water + MO (100 ppm) + Zn^{2+} (50 ppm)	
	CR (mdd)	CR (mdd)	IE (%)
1	59.09	1.18	98
3	21.52	0.86	96
5	14.9	1.94	87
7	17.0	2.89	83

Table 4—Influence of various pH on the inhibition efficiency of MO– Zn^{2+} system
Immersion period: One day

pH	System		
	Well water	Well water + MO (100 ppm) + Zn^{2+} (50 ppm)	
	CR (mdd)	CR (mdd)	IE (%)
6	17.27	6.22	64
8	59.09	1.18	98
11	3.64	0.51	86

to the fact that zinc ions in the bulk of the solution are precipitated as zinc hydroxide.

Analysis of polarization curves

The potentio dynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. 2. The corrosion parameters are given in Table 5. When carbon steel was immersed in well water the corrosion potential was -550 mV versus SCE. The corrosion current was 52.480×10^{-5} A/cm^2. When MO (100 ppm) and Zn^{2+} (50 ppm) were added to the above system, the corrosion potential shifted to -557 mV versus SCE. The equal tafel slopes (b_a and b_c) indicate that the formulation consisting of MO and Zn^{2+} functions as a mixed inhibitor. In the presence of this inhibitor system, the corrosion current decreased from 52.480×10^{-5} to 2.5118×10^{-5} A/cm^2. This suggests the inhibitive nature of this inhibitor system.

Analysis of FTIR spectra

The FTIR spectra of pure methyl orange and the MO-Fe^{2+} (prepared by mixing MO and freshly prepared FeSO$_4$ and dried) are shown in Fig. 3a and 3b, respectively. Analysis of the two spectra shows that there is shift in –S=O symmetric stretching frequency from 1120 to 1111 cm^{-1}; the –N=N– shifts from 1421 to 1383 cm^{-1}. The aromatic C=C ring stretching frequency shifts from 1608 to 1641 cm^{-1} and C-N stretching frequency shifts from 1367 to

Table 5—Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitors

Inhibitor : MO (100 ppm) + Zn^{2+} (50 ppm)

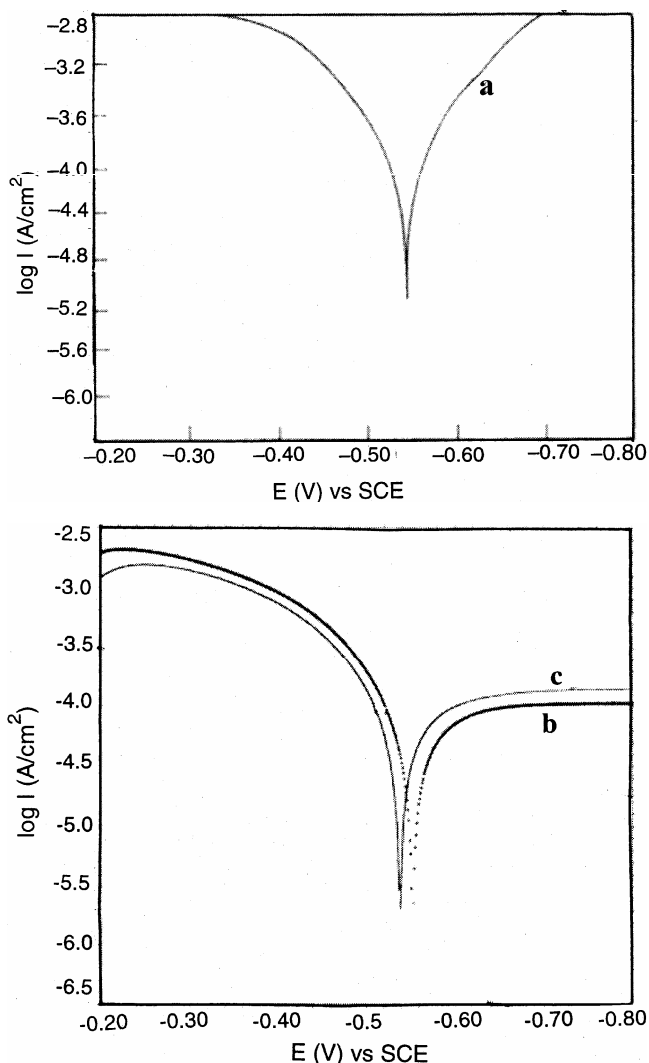| MO (ppm)	Zn^{2+} (ppm)	E_{corr} (mV) vs SCE	b_a (mV)	b_c (mV)	I_{corr} (A/cm^2)
0	0	-550	115	125	52.480 x 10^{-5}
100	0	-553	139	60.7	3.3597 x 10^{-5}
100	50	-557	64	64	2.5118 x 10^{-5}

Fig. 2—Polarization curves of carbon steel immersed in test solution. (a) well water, (b) well water + MO (100 ppm), and (c) well water + MO (100 ppm) + Zn^{2+} (50 ppm)

1383 cm^{-1}. These observations suggest that MO forms complex with Fe^{2+} by co-ordinating through oxygen atom of the sulphonic acid group, nitrogen atom of the azo group, the aromatic pi electrons and the nitrogen atom of the –N (CH$_3$)$_2$ in methyl orange[27].
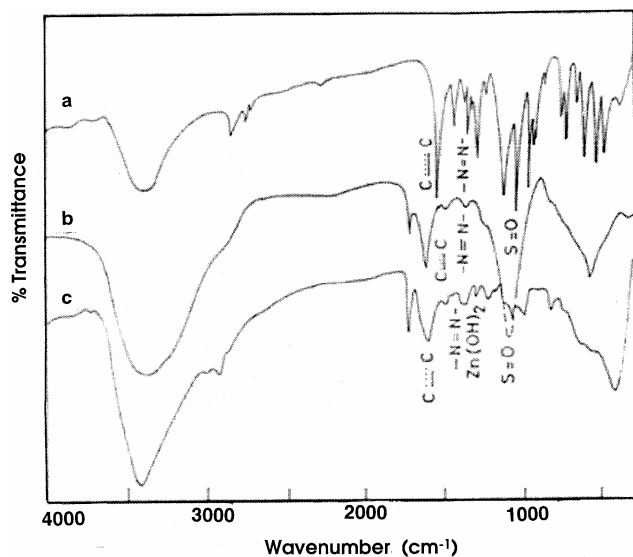
Fig. 3—FTIR Spectra of (a) Pure MO, (b) Prepareed Fe^{2+}-MO complex, and (c) Film formed on the surface of carbon steel when immersed in 100 ppm MO + 50ppm Zn^{2+} solution

The FTIR spectrum of the film formed on the surface of the carbon steel after immersion in solution containing MO (100 ppm) and Zn^{2+} (50 ppm) is shown in Fig. 3c. The $-S = O$ symmetric stretching frequency has shifted from 1120 to 1113 cm^{-1}. The $-N=N-$ has shifted from 1421 to 1392 cm^{-1}. The aromatic C=C ring stretching frequency has shifted from 1608 to 1628 cm^{-1}. The C-N stretching frequency has shifted from 1367 to 1392 cm^{-1}. Spectrum shown in Fig. 3b is almost identical with spectrum shown in Fig. 3c. This confirms that the complex formed on the carbon steel under this study is identical with the complex prepared. The peak at 1350 cm^{-1} is due to zinc hydroxide[27,28].

Mechanism of corrosion inhibition

In view of the above results, the following mechanism may be proposed for the corrosion inhibition of carbon steel immersed in well water:

(i) The formulation consisting of 100 ppm of MO and 50 ppm of Zn^{2+} in well water contains MO–Zn^{2+} complex in solution.

(ii) When carbon steel is immersed in this solution MO–Zn^{2+} complex diffuses from the bulk of the solution to the metal surface.

(iii) MO-Zn^{2+} complex is converted into MO–Fe^{2+} complex (as it is more stable than MO-Zn^{2+} complex) on the anodic sites of the metal surface with the release of zinc ion.

$$Zn^{2+} - MO + Fe^{2+} \rightarrow Fe^{2+} - MO + Zn^{2+}$$
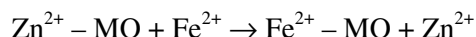
(iv) The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$$
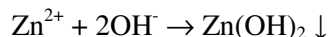
(v) Thus, the protective film consists of MO-Fe^{2+} complex and $Zn(OH)_2$.

(vi) In near neutral aqueous solution, the anodic reaction is the formation of Fe^{2+}. This anodic reaction is controlled by the formation of MO – Fe^{2+} complex on the anodic site of the metal surface. The cathodic reaction is the generation of OH^-, which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface.

$Fe \rightarrow Fe^{2+} + 2e^-$ (Anodic reaction)

$2H_2O + O_2 + 4e^- \rightarrow 4\ OH^-$ (Cathodic reaction)
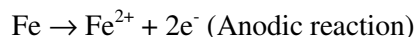
This accounts for the synergistic effect of MO–Zn^{2+} system.

Conclusion

Methyl orange along with Zn^{2+} acts as a corrosion inhibitor system for carbon steel in well water. Its efficiency increased due to the transporting ability of zinc ion through the formation of the MO-Zn^{2+} complex. The IE of 100 ppm MO + 50 ppm Zn^{2+} system is found to decrease as the immersion period increases. A suitable mechanism has been proposed for the corrosion inhibition based on the results of polarization study and FTIR spectra. The protective film consists of Fe^{2+}-MO complex formed on the anodic sites and $Zn(OH)_2$ on the cathodic sites of the metal surface. This confirms that MO – Zn^{2+} system functions as a mixed inhibitor system.

Acknowledgement

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