CORROSION INHIBITION BY CARBOXYMETHYL CELLULOSE

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The inhibition efficiency (IE) of carboxymethyl cellulose (CMC)-Zn^{2+} system in controlling corrosion of carbon steel in ground water in the absence and presence of Zn^{2+}has been evaluated by weight loss method. The formulation consisting of 250 ppm CMC and 50 ppm Zn^{2+} has 98 % IE. A synergistic effect exists between CMC and Zn^{2+}. Synergism has been confirmed by synergism parameter. AC impedance spectra confirm the formation of protective film on the metal surface. The nature of the protective film has been characterized by scanning electron microscopy (SEM).

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INTRODUCTION

Corrosion can be defined as the destruction of metals and alloys by electrochemical reaction with its environment. Corrosion occurs because of the natural tendency of the metals to return back to their thermodynamically stable native state. It cannot be avoided, but it can be controlled and prevented by using appropriate preventive measures like cathodic protection, anodic protection, coating, alloying and using inhibitors, etc. Out of these methods, the inhibitors reduce the aggressiveness of the corrosion and harmful aqueous environment. Thus prevent the metal and alloy by the forming of a protective layer on the metal surface. The applications of inhibitors are mostly find applications in cooling water system and boiler water system.[1,2] The organic compounds containing hetero atoms like oxygen, nitrogen, phosphorus, halogen and sulphur, etc have been used as corrosion inhibitors to control the metals from corrosion.[3-5] The compound carboxy methyl cellulose,[6-8] has been used as corrosion inhibitor for mild steel in various aqueous environments. Rajendran *et al.* have been investigated that the corrosion behavior of carbon steel in presence of carboxymethyl cellulose-1-hydroxyethane-1,1-diphosphonic acid.[9] Moreover, the application of polymers and their derivatives in corrosion controlling of metals and alloys in various aqueous environment have been investigated by various researchers.[10-11]

The present work is undertaken:

1) to evaluate the inhibition efficiency(IE) of CMC in controlling corrosion of carbon steel in ground water which is collected from Yadava college which is located at Madurai, Tamil Nadu, India (**Table 1**)

2) to study the synergism using synergism parameters.

3) to understand the mechanistic aspects of corrosion inhibition and formation of protective film on the metal surface by AC impedance spectra.

4) to analyze the protective film formed on the metals surface by scanning electron microscopy (SEM)

5) to propose a suitable mechanism for corrosion inhibition process.

EXPERIMENTAL

Preparation of the specimens

Carbon steel specimens (0.026 % S, 0.06 % P, 0.40 % Mn, 0.10 % C, and the rest iron) of dimensions 1.0 x 4.0 x0.2 cm were polished to mirror finish and degreased with trichloroethylene were used for both weight-loss method and surface examination studies. The environment chosen is ground water and the physico-chemical parameter of ground water is given in **Table 1**.

Table 1. Physico-chemical parameters of ground water

Parameters	Value
pH	7.3
Total Hardness as $CaCO_3$	460 ppm
Calcium	32 ppm
Magnesium	91 ppm
Nitrate	8 ppm
Chloride	270 ppm
Fluoride	0.8 ppm
Sulphate	100 ppm
Phosphate	0.46 ppm

Weight- loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the ground water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for 3 day. The corrosion product was cleaned with Clark's solution.[12] The weights of the specimens before and after immersion were determined using an analytical balance, Shimadzu AY210 model. Then the Inhibition efficiency (*IE*) was calculated using the equation (1).

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

where

W_1=corrosion rate (mdd) in absence of inhibitor,

W_2 = corrosion rate (mdd) in presence of inhibitor.

The corrosion rate (*CR*, in mdd) was calculated using the equation (2)

$$CR = \frac{\Delta m}{A t} \quad (2)$$

where

Δm - weight loss in mg

A- area of the specimen in dm^2

t- Immersion period in days

Synergism Parameter (S_I)

Synergism parameters are indications of synergistic effect existing between the inhibitors. S_I value is found to be greater than one suggesting that the synergistic effect between the inhibitors.[13-14] The S_I value can be calculated using the formula as follows:

$$S_I = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}} \quad (3)$$

where,

$\theta_{1+2} = (\theta_1+\theta_2) - (\theta_1\theta_2)$

θ_1 = surface coverage of inhibitor CMC

θ_2 = surface coverage of inhibitor Zn^{2+}

θ'_{1+2} = combined surface coverage of inhibitor carboxymethyl cellulose (CMC) and Zn^{2+}.

AC impedance measurements

AC Impedance study was carried out in Electrochemical Impedance Analyzer model CHI 660A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrode. AC impedance spectra were recorded after doing iR compensation. The real part (*Z*') and imaginary part (*Z*'') of the cell impedance were measured in ohms for various frequencies. The corrosion parameters such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated. During the AC impedance spectra, the scan rate (V s^{-1}) was 0.005; Hold time at Ef (s) was zero and quiet time (s) was 2.

Surface Characterization by Scanning Electron Microscopy (SEM)

The carbon steel immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of the carbon steel were examined using HITACHI S-3000 H computer controlled scanning electron microscope.

RESULTS AND DISCUSSION

Analysis of results of weight loss study

The calculated inhibition efficiencies (*IE*) and corrosion rates (*CR*) of CMC in controlling corrosion of carbon steel immersed in ground water both in the absence and presence of Zn^{2+} ion are given in **Table 2**.

Table 2: Inhibition efficiencies (IE %) and Corrosion rates (CR) obtained from CMC - Zn^{2+} systems, when carbon steel is immersed in ground water

CMC ppm	Zn^{2+}, ppm			
	0		50	
	***CR*, mdd**	***IE* %**	***CR*, mdd**	***IE*, %**
0	15.15	---	12.88	15
25	13.64	10	5.30	65
50	12.57	17	3.64	76
75	11.51	24	2.12	86
100	9.85	35	1.52	90
125	8.33	45	0.91	94
250	7.88	48	0.30	98

The calculated values indicate the ability of CMC to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of Zn^{2+} ion. CMC alone shows some IE. But the combination of 250 ppm CMC and 50 ppm Zn^{2+} shows 98% IE. This suggests that a synergistic effect exists between CMC and Zn^{2+} ion.[15-20]

Synergism parameters (S_I)

The synergism parameters of CMC-Zn^{2+} system are given in **Table 3**. For different concentrations of inhibitors, S_I approaches 1 when no interaction between the inhibitor compounds exists. When S_I >1, it points to synergistic effects. In the case of S_I<1, it is an indication that the synergistic effect is not significant. From Table 4, it is observed that value of synergism parameters (S_1) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between CMC and Zn^{2+} ions.[21]

Table 3: Inhibition efficiencies and synergism parameters for various concentrations of CMC-Zn^{2+} system, when carbon steel immersed in ground water

CMC, ppm	25	50	75	100	125	250
θ_1	0.10	0.17	0.24	0.35	0.45	0.48
θ_2 (Zn^{2+}= 5 ppm)	0.07	0.07	0.07	0.07	0.07	0.07
θ_{1+2}	0.16	0.23	0.29	0.42	0.49	0.52
θ'_{1+2}	0.20	0.35	0.55	0.60	0.70	0.75
S_I	1.05	1.19	1.57	1.51	1.71	1.93
θ_1	0.10	0.17	0.24	0.35	0.45	0.48
θ_2 (Zn^{2+}= 10 ppm)	0.10	0.10	0.10	0.10	0.10	0.10
θ_{1+2}	0.19	0.25	0.32	0.42	0.51	0.53
θ'_{1+2}	0.44	0.56	0.76	0.88	0.89	0.90
S_I	1.45	1.69	2.85	4.88	4.50	4.68
θ_1	0.10	0.17	0.24	0.35	0.45	0.48
θ_2 (Zn^{2+}= 25 ppm)	0.12	0.12	0.12	0.12	0.12	0.12
θ_{1+2}	0.21	0.27	0.33	0.43	0.52	0.54
θ'_{1+2}	0.50	0.70	0.80	0.82	0.90	094
S_I	1.58	2.43	3.34	3.17	4.84	7.63
θ_1	0.10	0.17	0.24	0.35	0.45	0.48
θ_2 (Zn^{2+}= 50 ppm)	0.15	0.15	0.15	0.15	0.15	0.15
θ_{1+2}	0.24	0.29	0.35	0.45	0.53	0.56
θ'_{1+2}	0.65	0.76	0.86	0.90	0.94	0.98
S_I	2.19	2.94	4.41	5.53	7.79	22.1

Analysis of AC impedance spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases and the impedance log(Z/ohm) value increases. The AC impedance spectra of carbon steel immersed in ground water in the absence and presence of inhibitors (CMC-Zn^{2+}) are shown in **Fig.1** to **Fig. 3**. The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in **Table 4**. The impedance value log (Z/ohm) derived from Bode plots are also given in **Table 4**.

Table 4. Impedance parameters for corrosion of carbon steel immersed in ground water in the absence and presence of inhibitors obtained by AC impedance spectra

System	Nyquist plot		Bode plot
	R_t, Ω cm^2	C_{dl}, F cm^{-2}	log (Z/ohm)
Ground Water	1962.3	2.5989×10^{-9}	3.297
Ground Water + CMC (250 ppm) + Zn^{2+} (50 ppm)	2081.9	2.4496×10^{-9}	3.340

It is observed that when the inhibitors [CMC (250 ppm) + Zn^{2+} (50 ppm)] are added, the charge transfer resistance (R_t) increase from 1962.3 ohm cm^2 to 2081.9 ohmcm^2. The C_{dl} value decreases from 2.5989×10^{-9} Fcm^{-2} to 2.4496×10^{-9} F cm^{-2}. The impedance value [log(Z/ohm)] increases from 3.297 to 3.340. These results lead to the conclusion that a protective film is formed on the metal surface.[22-25]

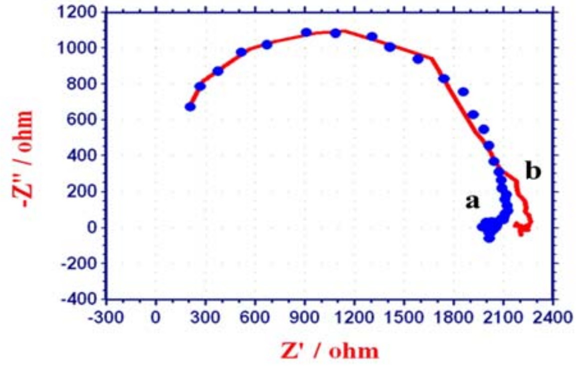

Figure 1. AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plot) a) Ground water b) Ground water + CMC (250 ppm) + Zn^{2+}(50 ppm)

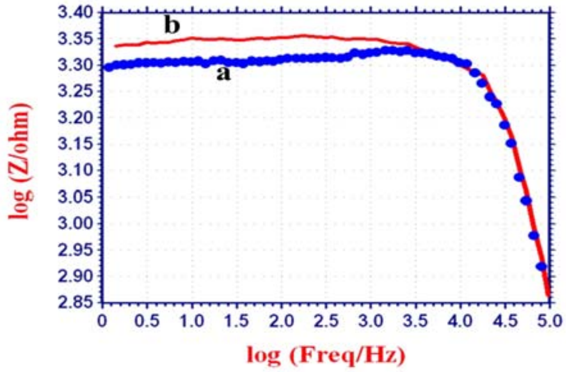

Figure 2. AC impedance spectra of carbon steel immersed in various testsolutions (impedance-Bode plot) a) Ground water (blank) b) Ground water + CMC (250 ppm) + Zn^{2+}(50 ppm)

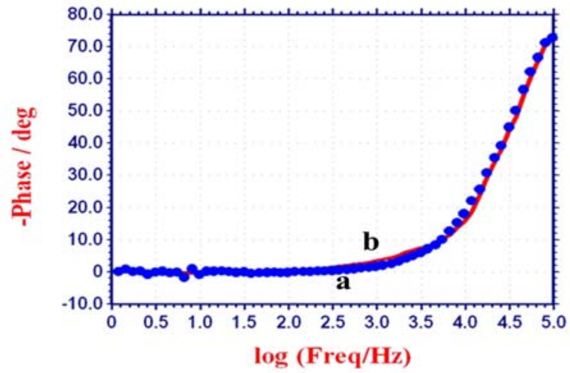

Figure 3. AC impedance spectra of carbon steel immersed in various testsolutions (Phase-Bode plot) a) Ground water, b) Ground water + CMC (250 ppm) + Zn^{2+} (50 ppm)

Scanning Electron Microscopy (SEM)

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined.[26] The SEM micrograph (X 500) of a polished carbon steel surface (control) in **Fig. 4 (a)** shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface.

The SEM micrograph (X 500) of carbon steel specimen immersed in the ground water for one day is shown **in Fig. 4 (b)** and **(c)** respectively. The SEM micrograph of carbon steel surface immersed in ground water in **Fig. 4 (b)** shows the roughness of the metal surface which indicates the corrosion of carbon steel in ground water. The **Fig. 4 (c)** indicates that in the presence of 250 ppm CMC and 50 ppm Zn^{2+} mixture in ground water, the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface. In the presence of CMC and Zn^{2+}, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel.[27]

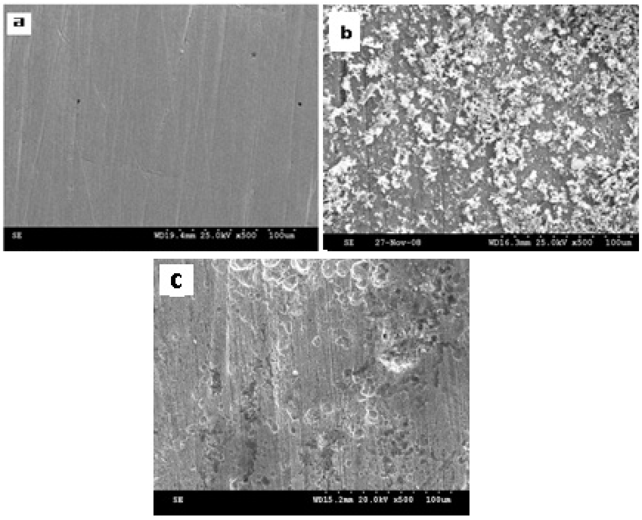

Figure 4. SEM analysis of a) Polished Carbon steel (control); b) Carbon steel immersed in ground water (Blank); c) Carbon steel immersed in ground water + 250 ppm of CMC + 50 ppm of Zn^{2+}

Mechanism of corrosion inhibition

Based on the above studies the following mechanism can be proposed for corrosion inhibition process.

$$Zn^{2+} - CMC + Fe^{2+} \rightarrow Fe^{2+} - CMC + Zn^{2+}$$

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

Protective film consists of Fe^{2+} - CMC complex and $Zn(OH)_2$

At anode: $Fe \rightarrow Fe^{2+} + 2e^-$

At cathode: $H_2O + ½\ O_2 + 2e^- \rightarrow 2\ OH^-$

$$Fe^{2+} - CMC \rightarrow CMC\ complex$$

It accounts for the synergism of CMC – Zn^{2+} system.

CONCLUSIONS

The present study leads to the following conclusions:

The formulation consists of 250 ppm of CMC and 50 ppm of Zn^{2+} offers 98% IE to carbon steel immersed in ground water.

Synergistic effect of exists between CMC and Zn^{2+}.

AC impedance spectra reveal that the formation of protective film on the metal surface.

SEM study confirms the formation of protective film on the metal surface and hence the corrosion process is inhibited.

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