

# EFFECT OF $Zn^{2+}$ ON CORROSION BEHAVIOUR OF CARBON STEEL IN EUCALYPTUS CAMALDULENSIS

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## Abstract:

The inhibition efficiency (IE) of Eucalyptus Camaldulensis Extract (ECE) in controlling corrosion of carbon steel in well water in the presence and absence of  $Zn^{2+}$  has been evaluated by weight loss method. The formulation consisting of 8 mL of Eucalyptus Camaldulensis Extract (ECE) and 5 ppm  $Zn^{2+}$  offers 98 % inhibition efficiency to carbon steel immersed in well water. Potentiodynamic polarization study reveals that this system formulation acts as mixed type inhibitor. AC impedance confirms that compact protective film is formed on the metal surface. The surface morphology of inhibited and uninhibited carbon steel is also analyzed by Scanning Electron Microscopy (SEM).

**Keywords:** Corrosion inhibition, Carbon steel, Eucalyptus Camaldulensis Extract.

## 1. INTRODUCTION:

Corrosion is degradation of materials properties due to interactions with their environments. Chloride, sulphate and nitrate ions in aqueous media are aggressive and accelerate corrosion [1]. Eco-friendly corrosion inhibitors are cheap, biodegradable and do not contain heavy metals or other toxic substances [2]. Several investigations have been reported using plant extracts of *Enicostemma axillare* [3], *Melia azadirachta* [4], *Cordia latifolia* [5], *Jasminum auriculatum* [6], *Hisbiscus Subdariffa* [7], *Canavalia ensiformis* [8], *Rosa Sinensis linn* [9], *Phyllophaora nervosa* [10], *Lawsonia* [11], *Pomegranate* [12], *Azadiractha Indica* [13] as green corrosion inhibitor for different metals in various media by several authors. In our present study, the inhibition efficiency of Eucalyptus Camaldulensis Extract (ECE) as corrosion inhibitor for carbon steel in well water is investigated on the basis of weight loss method, potentiodynamic polarization study, electrochemical technique and Scanning Electron Microscopy.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of the specimen

Carbon steel specimens of size 1.0 cm × 4.0 cm × 0.2 cm and chemical composition 0.026 % Sulphur, 0.06 % Phosphorous, 0.4 % Manganese, 0.1 % Carbon and the rest iron were polished to a mirror finish and degreased with trichloroethylene and used for the weight loss method and surface examination studies.

## 2.2. Preparation of Eucalyptus Camaldulensis Extract

An aqueous extract of Eucalyptus Camaldulensis was prepared by grinding 10g of shade dried Eucalyptus Camaldulensis leaves, with distilled water, filtering the suspending impurities, and making upto 100ml. The extract was used as corrosion inhibitor in the present study. The major active constituents present in Eucalyptus Camaldulensis is Eucalyptol (IUPAC: 1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octane)

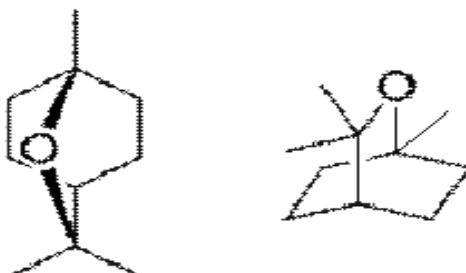


Fig.1. Structure of Eucalyptol

## 2.3. Corrosion medium

In our present study, well water chosen as corrosive media were collected from due well at Seelapadi, Dindigul.

**Table 1:** Physiochemical parameter of well water:

Parameters	Results
Appearance	Colorless
Total dissolved solids	1756 ppm
pH	7.62
Total hardness	730ppm
Calcium	152ppm
Magnesium	84ppm
Iron	0.85ppm
Conductivity	2582 Micro mho / cm
Chloride	475 ppm
Sulphates	14 ppm

## 2.4. Weight-loss method

Carbon steel specimens were immersed in well water containing various concentrations of the inhibitor Eucalyptus Camaldulensis extract (ECE) in the absence and presence of  $Zn^{2+}$  for one day. The weights of the specimens before and after immersion were determined using a Digital Balance (Model AUY 220 SHIMADZU).

The inhibition efficiency (IE) was then calculated using the equation:

$$IE (\%) = \left( \frac{W_0 - W_1}{W_0} \right) \times 100$$

Where,  $W_0$  is the weight loss value in the absence of inhibitor and  $W_1$  is the weight loss value in the presence of inhibitor.

From the change in weight of the specimens, corrosion rates (CR) were calculated with the help of the following relationship

$$CR = \frac{\Delta m}{A * T}$$

Where,

CR - corrosion rate

$\Delta m$  - loss in weight (mg)

A - Surface area of the specimen ( $\text{dm}^2$ )

T - Period of immersion (days)

## 2.5. Potentiodynamic Polarization

Polarization studies were carried out in a CHI- electrochemical work station with impedance model 660A. It was provided with iR compensation facility. A three electrode cell assembly was used. The working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study corrosion parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current ( $I_{\text{corr}}$ ), Tafel slopes anodic =  $b_a$  and cathodic =  $b_c$  were calculated and polarization study was done. The scan rate (V/S) was 0.01. Hold time at ( $E_{\text{fcs}}$ ) was zero and quiet time (s) was two.

## 2.6. AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part ( $Z'$ ) and imaginary part ( $Z''$ ) of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance ( $R_{\text{ct}}$ ) and the double layer capacitance ( $C_{\text{dl}}$ ) were calculated. AC impedance spectra were recorded with initial  $E(\text{v}) = 0$ , high frequency (Hz) =  $1 \times 10^5$ , low frequency (Hz) = 1, amplitude (V) = 0.005 and quiet time (s) = 2.

## 2.7. Scanning Electron Microscopy

The Surface morphology measurements of the carbon steel were examined after one day of immersion in test solution by using JEOL JSM 6390 model. All SEM micrographs of carbon steel are taken at a magnification of  $X=200$

### 3. RESULTS AND DISCUSSION

#### 3.1. Analysis of the results of the mass loss method

The calculated inhibition efficiencies (IE) of Eucalyptus Camaldulensis extract (ECE) 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 1. The formulation consisting of 8ml of ECE and 5 ppm of  $Zn^{2+}$  offers 98% inhibition efficiency. The calculated values indicate the ability of extract to be a good corrosion inhibitor. The inhibition efficiency is found to be enhanced in the presence of Zinc ion.

**Table 2:** Corrosion rates (CR) of carbon steel in well water in the absence and presence of inhibitors and the inhibition efficiencies obtained by mass loss method

Inhibitor system: ECE +  $Zn^{2+}$

Period of immersion: 1 day

ECE (ml)	$Zn^{2+}$ (0 ppm)		$Zn^{2+}$ (5 ppm)	
	IE (%)	CR (mdd)	IE (%)	CR (mdd)
0	--	59.09	15.00	75
2	41	35.00	14.55	75
4	63	21.82	14.55	75
6	65	20.91	12.73	78
8	77	13.62	0.90	98

#### 3.2. Analysis of polarization curves

A polarization study has been used to detect the formation of protective film on the metal surface [14-20]. When a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and the corrosion current ( $I_{corr}$ ) decreases. The potentiodynamic polarization curves of carbon steel immersed in various test solutions are shown in Fig.2. The corrosion parameters namely, corrosion potential ( $E_{corr}$ ), Tafel slopes ( $b_c$ = cathodic ;  $b_a$  = anodic ), linear polarization resistance (LPR) and corrosion current ( $I_{corr}$ ) are given in Table 3. when carbon steel is immersed in an aqueous solution containing well water, the corrosion potential is 272 mV vs SCE. The formulation consisting of 8 ml of Eucalyptus Camaldulensis extract (ECE) and 5 ppm of  $Zn^{2+}$  shifts the corrosion potential to 289 mV vs SCE. This suggests that the anodic reaction is controlled predominantly. The (LPR) value increases from  $1.06 \times 10^5$  ohm  $cm^2$  to  $1.34 \times 10^5$  ohm  $cm^2$ . This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from  $6.501 \times 10^{-9}$  A/  $cm^2$  to  $4.483 \times 10^{-9}$  A/  $cm^2$ . The IE

calculated from corrosion current is 79%. This value is lower than the IE obtained by weight loss method (98%). The discrepancy may be explained by the fact that in electrochemical processes, the instantaneous corrosion current is measured. However, in the case of weight loss method, IE is calculated after a long time. The protective film formed is strengthened as the duration of immersion increases.

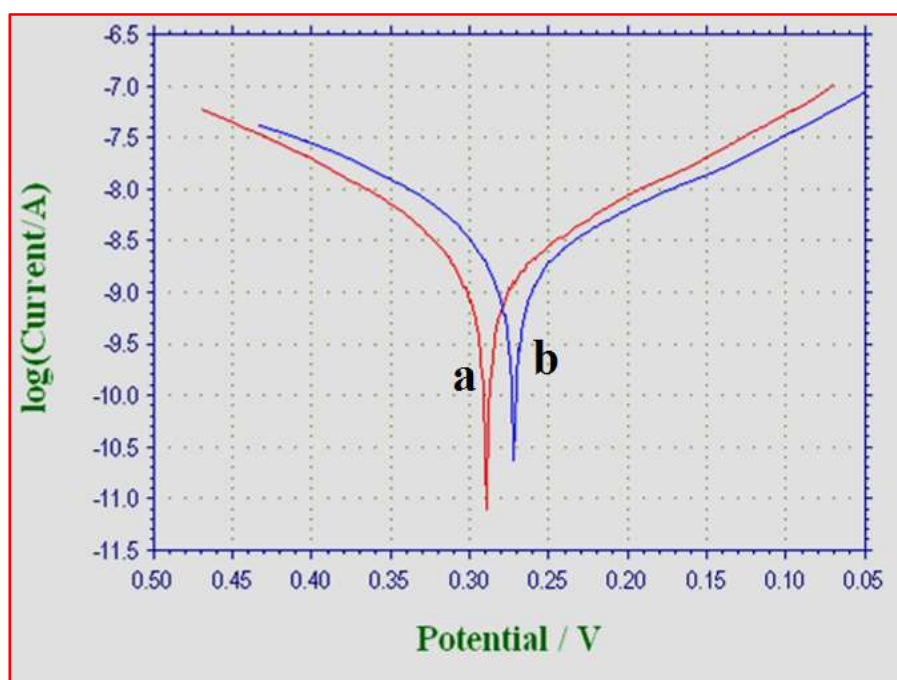


Fig.2. Polarization curves of carbon steel immersed in various test solution

- a) Well water
- b) Well water + ECE (8ml) + Zn<sup>2+</sup> (5ppm)

**Table 3:** Tafel polarization values for the corrosion of carbon steel in well water in the absence and presence of inhibitor formulation:

System	E <sub>corr</sub> (mV vs SCE)	b <sub>c</sub> (mV/dec)	b <sub>a</sub> (mV/dec)	LPR (Ohm cm <sup>2</sup> )	I <sub>corr</sub> (A/cm <sup>2</sup> )
Well Water	272	692	704	1.06×10 <sup>5</sup>	6.501×10 <sup>-9</sup>
ECE (8 ml) + Zn <sup>2+</sup> (5 ppm)	289	809	853	1.34×10 <sup>5</sup>	4.483×10 <sup>-9</sup>

### 3.3. AC impedance spectra

AC impedance spectra have been used to detect the formation of film on the metal

Surface. If a protective film is formed, the charge transfer resistance increases and double layer capacitance value decrease [21-24]. The AC impedance spectra of carbon steel immersed in various solutions are shown in Fig 3. The AC impedance parameter, namely charge transfer resistance (R<sub>t</sub>) and double layer capacitance (C<sub>dl</sub>) are given in Table 4.



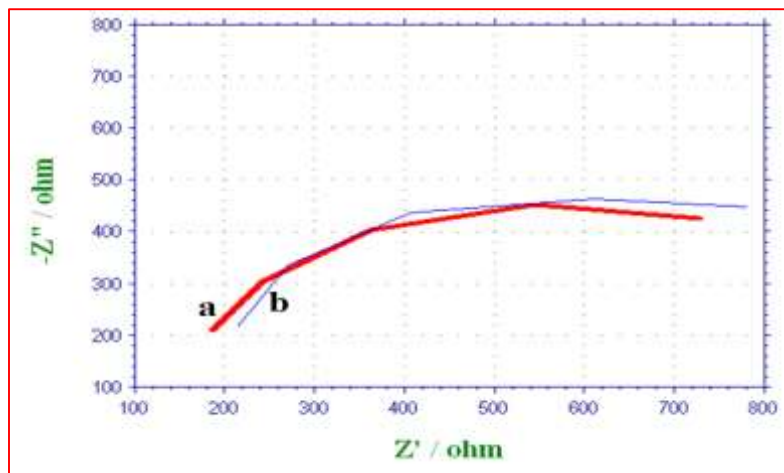


Fig.3. Impedance spectra of carbon steel immersed in various test solution

- a) Well water
- b) Well water + ECE (8ml) + Zn<sup>2+</sup> (5ppm)

When carbon steel is immersed in aqueous solution containing well water the  $R_t$  value is 544 ohm cm<sup>2</sup> and  $C_{dl}$  value  $9.375 \times 10^{-9}$  F/cm<sup>2</sup>. When ECE and Zn<sup>2+</sup> are added. The  $R_t$  value increases from 544 ohm cm<sup>2</sup> to 564 ohm cm<sup>2</sup> and  $C_{dl}$  value decrease from  $9.375 \times 10^{-9}$   $\mu$ F/cm<sup>2</sup> to  $9.0425 \times 10^{-9}$  F/cm<sup>2</sup>. This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of ECE - Zn<sup>2+</sup> system.

**Table 4:** AC impedance parameters of carbon steel immersed various test solution:

System	$R_t$ ( $\Omega$ cm <sup>2</sup> )	$C_{dl}$ ( $\mu$ F/cm <sup>2</sup> )
Well Water	544	$9.375 \times 10^{-9}$
ECE (8 ml) + Zn <sup>2+</sup> (5 ppm)	564	$9.0425 \times 10^{-9}$

### 3.4. Analysis of SEM

The SEM image of magnification (X200) of carbon steel specimen immersed in well water for one day in absence and presence of inhibitor are shown in figure 4. The SEM micrograph, of polished carbon steel (control) in figure 4 a shows the smooth surface of the metal. This shows the absence of any corrosion products formed on the surface. The SEM micrograph of carbon steel surface immersed in well water in figure 4 b. shows the roughness of the metal surface which indicates the corrosion of carbon steel in well water. Figure 4 c indicates that in the presence of 8 ml of ECE and 5 ppm of Zn<sup>2+</sup> mixture in water, the

surface coverage increases which in turn results in the formation of insoluble complex on the metal surface covered by a thin layer of inhibition which effectively controls the dissolution of the carbon steel [25].

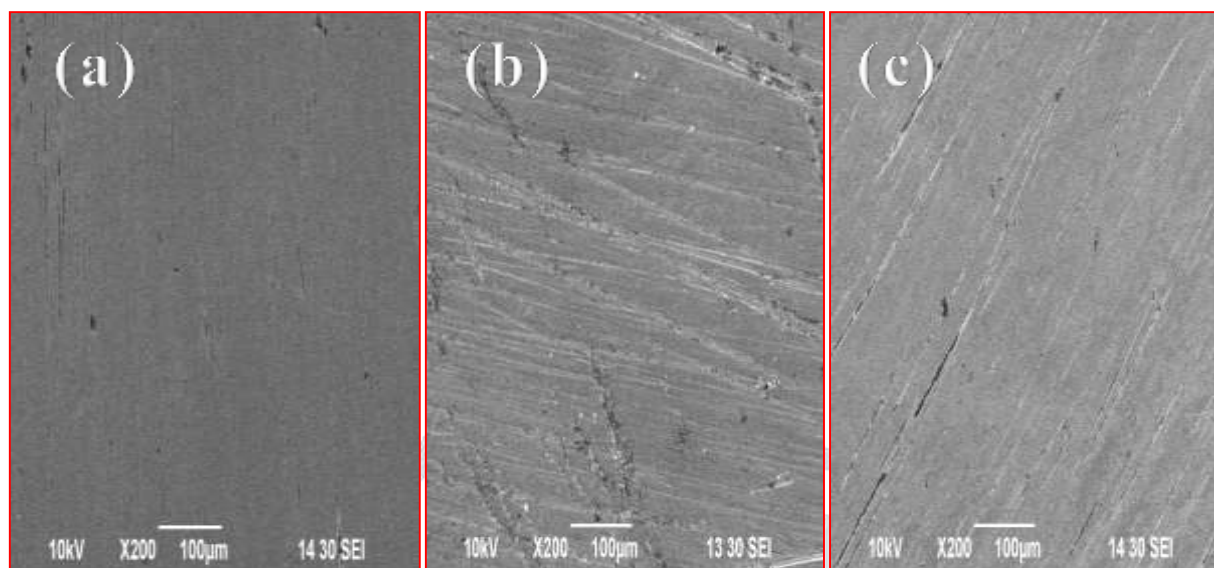


Fig.4. SEM images of

- a) Polished carbon steel
- b) carbon steel immersed in well water
- c) carbon steel immersed in well water + ECE (8 ml) +  $Zn^{2+}$  (5 ppm)

#### 4. CONCLUSION:

The present study leads to the following conclusion.

- ✓ Weight loss study reveals that the formulation consisting of 8 ml of ECE and 5 ppm of  $Zn^{2+}$  has 98% inhibition efficiency in controlling corrosion of carbon steel immersed in an aqueous solution of ECE.
- ✓ Polarization study reveals that this system functions as mixed type of inhibitor controlling the cathodic reaction and anodic reaction to equal extents.
- ✓ AC Impedance spectra reveal that a protective film is formed on the metal surface.
- ✓ The SEM study proves the protective film formed on the metal surface.

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