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Inhibition effect of glycine towards the corrosion of mild steel

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Abstract : Inhibition effect of glycine towards the corrosion of mild steel was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. It was found that these investigated compounds act as good inhibitors for the corrosion of mild steel in 250 ppm of glycine and 50 ppm of Zn^{2+}. EIS was used to investigate the mechanism of corrosion inhibition. The addition of Zn^{2+} was found to have a synergistic effect which enhanced the inhibition efficiency.

Keywords : Corrosion, mild steel, glycine, Zn^{2+}.

Introduction

Amino acids form a class of non toxic organic compounds. These properties would justify their use as corrosion inhibitors. The inhibitors are used in protection against the corrosion of certain metals such as nickel, cobalt, copper, iron and steel. All amino acids have a central or alpha carbon, to which are bonded four groups; hydrogen, an amino, a carboxyl group, and a unique side chain, also known as R-group[1,2]. The adsorption of amino acid on carbon steel in acidic environment has been investigated by Akiyama and Nobe[3]. Additional amino group or groups which increased electron density on the alpha amino group also increased the inhibition efficiency[4]. These molecules differ in their unique side chain, which can be used to classify the molecules into functional types. Cystein, alanine and phenylalanine have been used to inhibit the corrosion of bronze in an aqueous solution containing sodium sulphate and sodium bicarbonate[5-8]. Cystein, glycine, glutamic acid and glutathione have been used as corrosion inhibitor to prevent the corrosion of copper in HCl[9]. The corrosion of brass in O_2-free NaOH has been prevented by methionine[10]. Amino acids have been used to prevent chloride-induced corrosion in reinforced concrete structure[11,12]. Amino acids such as phenylalanine have been used to prevent corrosion of Mg-Al-Zn alloy in chloride-free neutral solution[13]. The electrochemical behaviour of cysteine has been studied by cyclic voltammetry[14,15]. Glycine dimethyl phosphonic acid is mainly used as corrosion inhibitor for industrial circulating cool water system. It is a new kind of organophosphine corrosion inhibitor. It shows certain antiscale ability and better corrosion inhibition as there are both carboxyl group and nitrogen phosphorus atoms in it. The aim of this research is to investigate the inhibitive effect of amino acid such as glycine. For this purpose potentiodynamic polarization and impedance spectroscopy have been used in the present study.

The present work is undertaken :

(i) To evaluate the inhibition efficiency of glycine in controlling corrosion of mild steel in an aqueous solution by weight loss methods.

(ii) To correlate the ligand-transporting efficiency of Zn^{2+} and the corrosion inhibition efficiency of glycine.

(iii) To study the mechanistic aspect of corrosion inhibition by electrochemical studies such as polarization study, AC impedance spectra.

(iv) To propose suitable mechanism of corrosion inhibition based on the above results.

Experimental

Preparation of specimens :

Preparations of the mild steel specimens were chosen from the same sheet of the following composition 0.1% C, 0.026% S, 0.06% P, 0.4% Mn and the balance Fe. Mild steel specimen of the dimensions 1.0 × 4.0 × 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass loss and electrochemical studies.

Weight loss study :

The weighed specimen in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of double distilled water in various concentration of inhibitors in the presence and absence of Zn^{2+} for 3 days of immersion. After 3 days of immersion the specimens were taken out, washed in running water dried and weighed. From the change in weights of the specimen corrosion rates were calculated using the following relationship,

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2) \times \text{Period of immersion (days)}} \quad (1)$$

Corrosion inhibition efficiency (IE) was then calculated using the equation,

$$\text{IE} = 100[1 - W_2/W_1]\% \quad (2)$$

where W_1 = corrosion rate in the absence of the inhibitors and W_2 = corrosion rate in the presence of the inhibitors.

Electrochemical study :

Polarization studies carried out in a CHI electrochemical workstation with impedance, Model 660 A, a three electrode cell assembly was used. The working electrode was one of the three metals. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode from the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = b_a and cathodic = b_c) were calculated.

AC impedance measurements :

EG and G electrochemical impedance analyser model 6310 was used to record AC impedance measurements. A three electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A rectangular platinum foil was used as the counter electrodes. A time interval of 5 to 10 min was given for the system circuit potential. There over this steady state potential an AC potential of 10 mV was superimposed. The AC frequency was varied from 100 MHz to KHz, the real part (Z') and imaginary part (Z'') of the cell impedance were measure in ohm for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. C_{dl} values were calculated using the following relationship,

$$C_{dl} = \frac{1}{2 \times 3.14 \times f_{max}} \quad (3)$$

Results and discussion

Analysis of results of weight loss methods :

Corrosion rates of mild steel immersed in an aqueous solution in the presence of glycine and Zn^{2+}, obtained by weight loss method as given in Tables 1 to 3. The inhibition efficiencies are also given in these tables. The

Table 1. Corrosion rates (CR) of mild steel immersed in DD water and the inhibition efficiencies (IE) obtained by weight loss method

Inhibitor : Glycine + Zn^{2+}

Glycine (ppm)	Zn^{2+}	CR (mdd)	IE (%)
0	0	30.25	–
50	0	25.7	15
100	0	23.8	21
150	0	13.37	56
200	0	11.19	63
250	0	9.98	67

Table 2. Corrosion rates (CR) of mild steel immersed in DD water and the inhibition efficiencies (IE) obtained by weight loss method

Inhibitor : Glycine + Zn^{2+}

Glycine (ppm)	Zn^{2+}	CR (mdd)	IE (%)
0	0	30.25	–
0	25	25.41	16
50	25	17.54	42
100	25	15.75	48
150	25	15.42	49
200	25	10.58	65
250	25	8.47	72

Table 3. Corrosion rates (CR) of mild steel immersed in DD water and the inhibition efficiencies (IE) obtained by weight loss method

Inhibitor : Glycine + Zn^{2+}

Glycine (ppm)	Zn^{2+}	CR (mdd)	IE (%)
0	0	30.25	–
0	50	28.13	7
50	50	13.31	56
100	50	11.49	62
150	50	9.07	70
200	50	6.65	78
250	50	4.84	84

corrosion rates of carbon steel as a function of concentration of inhibitors system are shown in Fig. 1. It is observed that when mild steel is immersed in double distilled water, the corrosion rate is 30.25 mdd. Upon addition of various concentration of glycine the corrosion rate slowly decreases. 250 ppm of glycine has 67% IE.

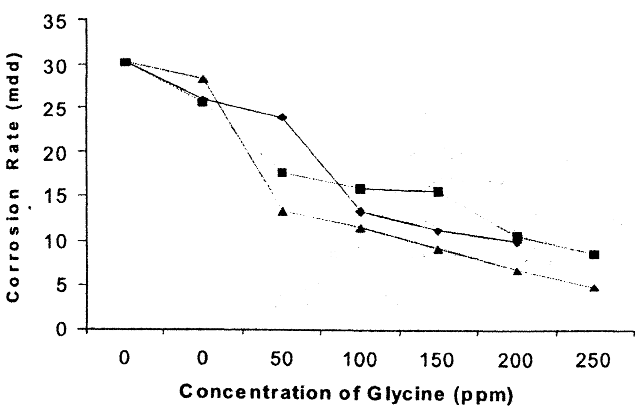

Fig. 1. Corrosion rates of mild steel as a function of concentration of glycine.

Influence of Zn^{2+} on the inhibition efficiency of glycine :

The influence of a divalent metal in Zn^{2+} on the efficiency of glycine in controlling corrosion of carbon steel given in Tables 2 and 3. It is observed that in the presence of 25 ppm of Zn^{2+} the IE of glycine slightly improves. The divalent Zn^{2+} ion form a complex with glycine, diffuses towards the metal surface and form Fe^{2+}-glycine complex releasing Zn^{2+}.

In the presence of 50 ppm of Zn^{2+}, the inhibition efficiency of glycine still increases. This is due to the fact that mono glycine is transported towards metal surface increases the formation of Fe^{2+}-glycine complex and hence an increase in the IE is noticed.

Analysis of polarization curves :

Analysis of results of potentiodynamic polarization study :

Polarization study has been used to study the formation of protective film on the metal surface[18] of carbon steel immersed in DD water in the absence and presence of inhibitors are shown in Fig. 2a.

The corrosion parameters namely corrosion potential (E_{corr}) Tafel slopes, b_c and b_a linear polarization resistance (LPR) and corrosion parameters (I_{corr}) are given in Table 4. It is observed that Fig. 1 when mild steel is immersed in double distilled water, the corrosion potential is –578 mV vs SCE (saturated calomel electrode). The LPR value is 1.46 $\times$ 10^3 Ω cm^2. The corrosion current value is 4.293 $\times$ 10^{-5} A/cm^2. When 250 ppm of glycine and 50 ppm of Zn^{2+} are added to the above environments the corrosion potential shifted to the anodic side (–443 mV vs SCE) (Fig. 2b).

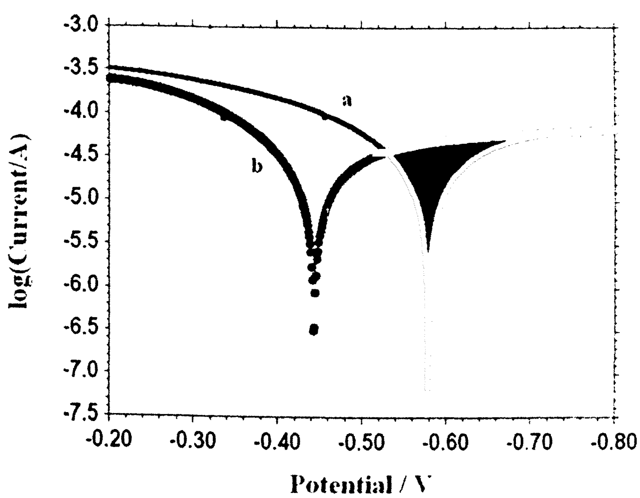

Fig. 2. Polarization curves of mild steel immersed in various test solutions : (a) DD water (blank), (b) glycine (250 ppm) + Zn^{2+} (50 ppm).

This indicates the corrosion potential is shifted to than ole side due to the formation of protective film on the metal surface. There is not much change in the value of cathodic Tafel slopes (221 and 200 mV/decade) but there is slight change in the anodic Tafel slope (415 and 412 mV/decade) this indicates that anodic reaction is con-

Table 4. Corrosion parameters of mild steel immersed in presence and absence of inhibitors from potentiodynamic polarization study

System	E_{corr} (mV vs SCE)	b_a (mV/decade)	b_c (mV/decade)	LPR (Ω cm^2)	I_{corr} (A/cm^2)
Double distilled water	–578	415	221	1.46×10^{-3}	4.293×10^{-5}
Double distilled water containing glycine (250 ppm) + Zn^{2+}	–443	412	200	1.55×10^{-3}	3.785×10^{-5}

trolled predominantly. Hence the glycine-Zn^{2+} system function as anodic inhibitor. It is observed from Table 5 that the LPR value increases and the corrosion current value decrease in presence of 250 ppm of glycine and 50 ppm of Zn^{2+}. There observation suggests the formation of a protective film on the metal surface. This prevents the corrosion of metal.

Analysis of AC impedance spectra :

AC impedance spectra of carbon steel immersed in double distilled water in the absence and presence of inhibitors are shown in Fig. 3 (Nyquist plot) and Fig. 4a,b (Bode plots). The corrosion parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in Table 5. The

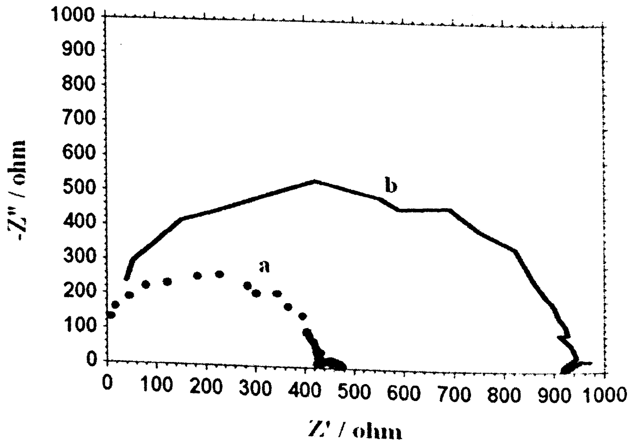

Fig. 3. AC impedance spectra of mild steel immersed in various test solutions (Nquist plot) : (a) DD water (blank), (b) glycine (250 ppm) + Zn^{2+} (50 ppm).

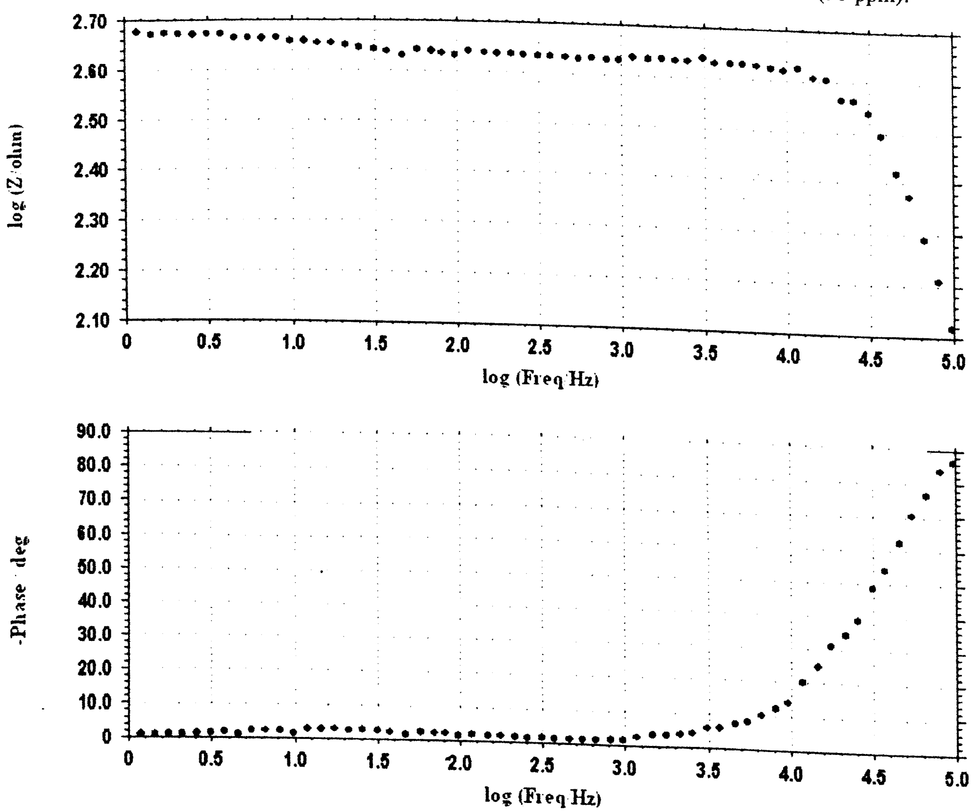

Fig. 4a. AC impedance spectra of mild steel immersed in various test solutions (Bode plot) : (a) DD water (blank).

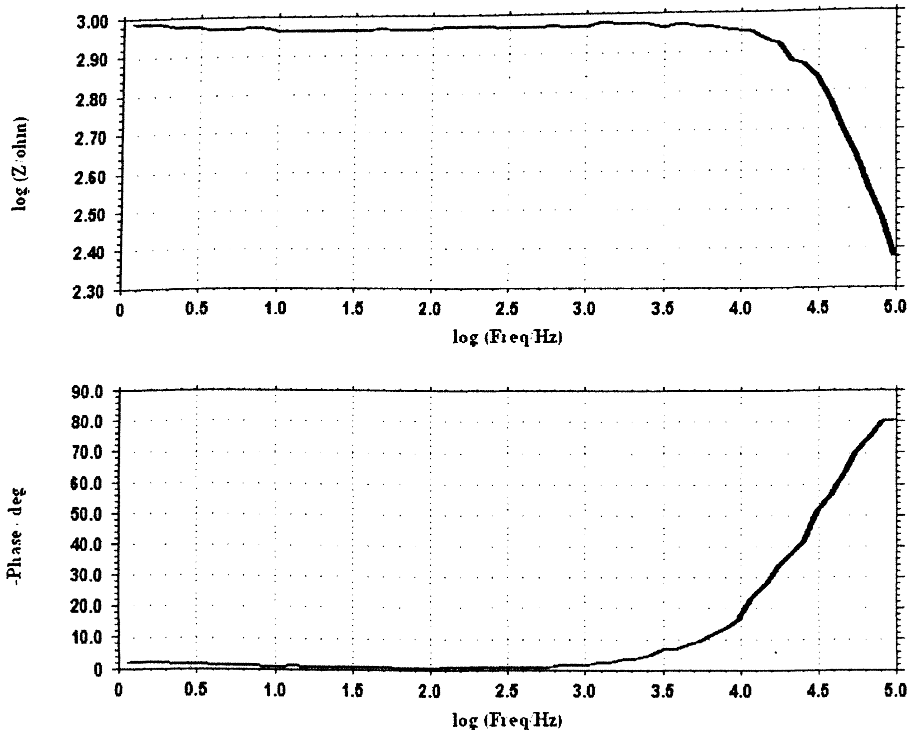

Fig. 4b. AC impedance spectra of mild steel immersed in various test solutions (Bode plot) : (a) glycine (250 ppm) + Zn^{2+}(50 ppm).

Table 5. Corrosion parameters of carbon steel immersed in double distilled water obtained from AC impedance spectra

System	R_t (Ω cm^2)	C_{dl} (F/cm^2)	Impedance [log (Z/Ω)]
Double distilled water	428	1.19×10^{-8}	2.683
Double distilled water containing 250 ppm of glycine + 50 ppm of Zn^{2+}	918	0.29×10^{-8}	2.992

impedance, log (Z/Ω) value derived from Bode plots are also given in Table 5. It is observed that when carbon steel in double distilled water, the R_t value is 428 Ω cm^2. The C_{dl} value is 1.19×10^{-8} F/cm^2. The impedance value [log (Z/Ω)] is 2.683. When inhibitors (250 ppm of glycine + 50 ppm of Zn^{2+}) are added the R_t value increases from 428 to 918 Ω cm^2. The impedance value increases from 2.683 to 2.992. This observation suggests that a protective film formed on the metal surface.

Mechanism of corrosion inhibition :

In order to explain the above fact in a holistic way the following mechanism of corrosion inhibition is proposed.

(i) When the formulation consisting of 250 ppm of glycine and 50 ppm of Zn^{2+} is prepared, there is formation of Zn^{2+}-glycine complex is solution.

(ii) When carbon steel metal is immersed in this solution, there is diffusion of Zn^{2+}-glycine complex towards the metal surface.

(iii) On the metal surface, it is converted to Fe^{2+}-glycine complex Zn^{2+} is released :

Zn^{2+}-Glycine + Fe^{2+} $\rightarrow$ Fe^{2+}-Glycine + Zn^{2+}.

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

(iv) Thus the protective film consists of Fe^{2+}-glycine complex and $Zn(OH)_2$.

Conclusion :

The inhibition efficiency of glycine-Zn^{2+} system in controlling corrosion of mild steel in double distilled water has been evaluated by weight loss method. The present study leads to the following conclusion. Weight loss study reveals that the formulation consisting of 250 ppm glycine and 50 ppm of Zn^{2+} has 84% inhibition efficiency polarization study reveals that this system function as a anodic inhibitor. So that glycine has suitable inhibitor to prevent corrosion in the industrial field. AC impedance spectra reveal that the protective film is formed on the metal surface. As the amount of Zn^{2+} ion available for transport of the ligand increases the inhibition efficiency increases.

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