



POLARIZATION STUDY OF CORROSION INHIBITION BY GLYCINE- Zn²⁺ SYSTEM

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The inhibition efficiency of glycine-Zn²⁺ system has been evaluated by weight loss method and polarization study. Glycine alone has some corrosion inhibition efficiency (IE). In presence of Zn²⁺, IE increases. Synergistic effects exist between Zn²⁺ and glycine. The formulation consisting of 250 ppm of glycine and 50 ppm of Zn²⁺ has 86% IE. Polarization study reveals that this system function as mixed inhibitor system, controlling the anodic reaction and cathodic reaction to an equal extent.

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acids will exist as zwitter ions, having both positive and negative charges. When an electric field is applied these ions will not move towards either the anode or the cathode. Hence these zwitter ions will be in the bulk of the solution. They will not be adsorbed on the metal surface. Hence their corrosion protection efficiency considerably decreases.

The present work is undertaken (i) to evaluate the corrosion inhibition efficiency of glycine in controlling corrosion of mild steel in an aqueous solution containing 60 ppm of Cl⁻, in the absence and presence of Zn²⁺ and (ii) to investigate the mechanistic aspects of corrosion inhibition by polarization study

Introduction

Metals are extracted from their ores by reduction process. When metals come in contact with the environment, especially oxygen and moisture, they deteriorate. This process, we call corrosion. Corrosion is the expression of desire of pure metals to go back to their original state of ores. Corrosion is a natural, spontaneous and thermodynamically stable process. The process of corrosion can be controlled but it cannot be prevented. There are many methods by which corrosion can be controlled.

One such method is the use of inhibitors. These inhibitors when added in small quantity, decrease the rate of corrosion. Corrosion inhibitors usually contain polar groups with atoms such as nitrogen, sulphur and oxygen. Correspondingly inhibitors include a wide list of organic and inorganic compounds containing the functional groups such as amines^{1,2} nitrocompounds^{3,4}, amides^{5,6} aldehydes^{7,8} ketones^{9,10} ester^{11,12} carboxylic acids^{13,14} thiocompounds^{15,16} phosphates^{17,18} phosphonates^{19,20} and amino acids.²¹⁻²⁵

Amino acids contain both carboxyl group and amino group. There are several amino acids. The simplest amino acid is glycine. Several amino acids such as valine,²⁶ glutamic acid,²⁷ phenyl alanine,³⁰ tyrosine,³¹ and tryptophan³² have been used as corrosion inhibitors. These corrosion inhibition efficiency is very much influenced by pH value of the medium since, under high pH value the carboxyl group will be in ionized form and under low pH value the carboxyl group will be in unionized form; but the amino group will be in protonated form. Interestingly, at isoelectric point amino

MATERIALS AND METHODS

Metal specimens

Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron. The dimension of the specimen was 1 x 4 x 0.2 cm

Weight-loss method:

Mild steel specimens in triplicate were immersed in 100 ml of aqueous solution containing 60 ppm of Cl⁻ in the presence and absence of Zn²⁺ and glycine for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution³³. The inhibition efficiency (IE) was then calculated using the

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

equation:

where

W₁ = corrosion rate in the absence of the inhibitor.

W₂ = corrosion rate in the presence of the inhibitor.

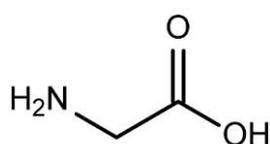
Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was mild steel. 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) and Linear polarization resistance (LPR) were calculated.

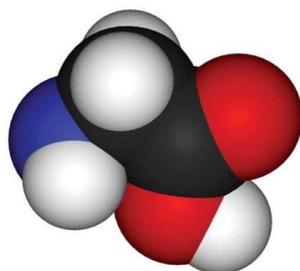
Results and Discussion

Analysis of weight loss method

The inhibition efficiency of glycine (Schemes 1 and 2) in controlling corrosion of mild steel immersed in an aqueous solution containing 60 ppm of Cl⁻ at pH 7.6 has been evaluated by weight loss method and polarization study, in the absence of and presence of Zn²⁺ ion.



Scheme 1. Molecular structure of glycine



Scheme 2. Space filling model of glycine

Corrosion rates of mild steel immersed in an aqueous solution containing 60 ppm of Cl⁻, in the absence and presence of Zn²⁺ are given in Table 1. The inhibition efficiencies are also given in this Table.

Table 1. Corrosion rates (CR) of mild steel immersed in an aqueous solution containing 60 ppm of Cl⁻ and the inhibition efficiency (IE) obtained by weight loss method

Glycine concentration, ppm	Zn ²⁺ concentration, ppm					
	0 ppm		25 ppm		50 ppm	
	CR	IE%	CR	IE%	CR	IE%
0	36	-	30.60	15	28.80	20
50	31.68	12	27.00	25	12.60	65
100	30.60	15	25.2	30	10.80	70
150	28.80	20	22.32	38	5.40	85
200	27.00	25	21.60	40	5.04	86
250	23.04	36	19.80	45	5.02	86

Immersion period: One Day; CR – Corrosion Rate (mdd), IE– Inhibition Efficiency

It is observed that glycine alone has some inhibition efficiency. As the concentration of glycine increases, IE also increases. 50 ppm of glycine has 12% IE and 250 ppm Glycine has 36% IE.

Influence of Zn²⁺ on inhibition efficiency of glycine

When Zn²⁺ (as ZnSO₄·7H₂O) is added to glycine system, the IE of glycine increases. This suggests that a synergistic effect exists between Zn²⁺ and glycine. Similar synergistic effect existing between Zn²⁺ and inhibitors has been reported by several researchers.³⁴⁻³⁸

The synergistic effect existing between Zn²⁺ and glycine can be explained as follows. When glycine and Zn²⁺ are mixed, Zn²⁺-glycine complex is formed. It is transported towards the metal surface. On the metal surface, Zn²⁺-glycine complex is broken. The released glycine combines with Fe²⁺ (formed on the metal surface due to corrosion process) resulting in the formation of Fe²⁺-glycine complex. Fe²⁺-glycine complex is more stable than Zn²⁺-glycine complex.³⁹⁻⁴³

Potentiodynamic polarization study

Corrosion is a problem facing us every day and in almost every activity. Corrosion wastes material and energy, and could prevent objects from doing the job they were made to do, possibly with dangerous consequences.

The rate at which corrosion occurs depends on the kinetics of the reactions taking place and so the **electrical double layer** is important.

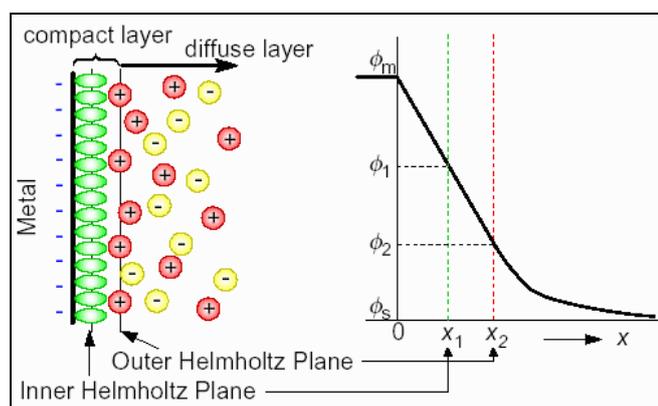
An electrical double layer is the name given to any region between two different phases when charge is separated across the interface between them.

In aqueous corrosion, this is the region between a corroding metal and the bulk of the aqueous environment (“free solution”). In the double layer, the water molecules of the solution align themselves with the electric field generated by applying a potential to the metal. In the Helmholtz model, there is a layer of aligned molecules (or ions), which is one particle thick and then immediately next to that, free solution. In later models (proposed by Louis Georges Gouy, David Leonard Chapman and Otto Stern) the layer is not well defined, and the orientation becomes gradually less noticeable further from the metal surface. However, for the purposes of determining the rate of corrosion, the Helmholtz model will suffice. To corrode, an ion in the metallic lattice must pass through the double layer and enter free solution. The double layer presents a potential barrier to the passage of ions and so has an acute effect on corrosion kinetics.

Helmholtz Double Layer

This theory is a simplest approximation that the surface charge is neutralized by opposite sign counter ions placed at an increment of d away from the surface.

The surface charge potential is linearly dissipated from the surface to the counterions satisfying the charge. The distance, d , will be that to the center of the counterions, i.e. their radius. The Helmholtz theoretical treatment does not adequately explain all the features, since it hypothesizes rigid layers of opposite charges. This does not occur in nature.



Scheme 3. Helmholtz Double Layer

If an electrode is at its equilibrium potential, both forwards and backwards reactions occur at the same rate, so no net reaction will occur. Net reactions only occur when the potential is moved away from equilibrium.

Kinetics of Corrosion - the Tafel Equation

Armed with the new Arrhenius expression and the generalized reaction:



where M is a metal that forms M^{z+} ions in solution, we can now derive an equation describing corrosion kinetics.

Consider the rate of the anodic (oxidation, corrosion) reaction, k_a

$$k_a = k_a' \exp\left(\frac{\Delta G^0}{RT}\right) \quad (3)$$

Since the reaction involves the release of electrons, its progress can be expressed as a current density, i (current per unit area).

The **exchange** current density, i_0 is defined as the current flowing in both directions per unit area when an electrode reaction is at equilibrium (and, hence, at its equilibrium potential).

If i_0 is small, then little current flows and the reactions at dynamic equilibrium are generally slow. Likewise, a high i_0 gives a fast reaction. The metal itself affects the value of i_0 , even if the reaction does not involve the metal directly.

$$i_0 = zFk_a = zFk_a' \exp\left(\frac{-\Delta G^0}{RT}\right) \quad (4)$$

If over potential is applied, the activation energy is changed.

$$i_a = i_0 \exp\left(\frac{\alpha zF\eta}{RT}\right) \quad (5)$$

This is one form of the **Tafel equation**. The Tafel equation can also be written in several equivalent ways. The quantity

$$\frac{2.303RT}{\alpha zF}$$

is given the symbol b_a and is known as the anodic Tafel slope. It has units of volts per decade of current.

Similarly, if the cathodic reaction were to be considered, the quantity would be

$$\frac{2.303RT}{(1-\alpha)zF}$$

since $(1-\alpha)$ is applicable instead of α and $E - E_e$ is negative. This quantity is the cathodic Tafel slope, b_c .

The usual form of Tafel's equation is

$$\eta = a + b_a \lg i_a \quad (6)$$

where

$$a = -\frac{2.303RT}{\alpha zF} \lg i_0 \quad (7)$$

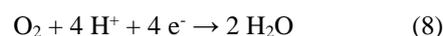
Through consideration of the reaction as both a chemical and electrical process and manipulation of algebra, it has been found that the applied potential is proportional to the log of the resulting corrosion current. This is certainly different to Ohmic behaviour where applied potential is directly proportional to the resulting current.

Corrosion occurs when two electrodes with different equilibrium potentials are in both electronic and electrolytic contact. Tafel plots can be used to predict corrosion rates.

Diffusion Limited Corrosion

So far all reactions have been assumed to proceed (if they are thermodynamically possible) at the rate predicted by the Tafel analysis. In reality, reactions are often limited by other factors and don't achieve this maximum rate. One such factor is the availability of oxygen in solution.

In aqueous solutions that contain dissolved oxygen, an important cathodic reaction is the oxygen reduction reaction:



The reaction takes place at the surface of the metal and so oxygen must be present at that site. If the reaction occurs quickly enough, the concentration of oxygen at the surface cannot be maintained at the same level as that in the bulk of the solution. In this case the rate of oxygen diffusion may become a limiting factor. With less oxygen available, the cathodic reaction slows down and so must the anodic reaction to conserve electrons (electrons can only be used up at the same rate as they are released as charge must always

be conserved). Fick's first law can be used to find the maximum rate of oxygen diffusion. Since each oxygen molecule consumes 4 electrons, according to the reaction above, this maximum rate of diffusion corresponds to a maximum current density that the oxygen reduction reaction can sustain and, hence, a maximum corrosion rate for the anode (since electrons must be used at the cathode at the same rate as they are released at the anode).

Since the corrosion current is limited, the cathodic arm of the Tafel plot is flattened:

Oxygen reduction is not the only process that deviates from the Tafel analysis. The hydrogen evolution reaction can be limited by the rate at which molecules desorb from the cathode surface. This is usually the rate-determining factor for hydrogen evolution on iron, copper, platinum and other metals. Relatively few metals behave as predicted by the Tafel analysis, examples being cadmium, mercury and lead.

Passivation

Another effect that limits the rate of corrosion is **passivation**. If the potential of an electrode is raised above some **passivation potential**, a passive product may become favorable forming a layer on the surface of the anode. In this case, the rate of corrosion can be much reduced. This is characterized by the value of $\log(i)$ peaking at a **critical current density**, before falling to some lower value.

In other words, the anodic arm of the Tafel plot reaches a peak and falls away to a roughly horizontal region:

Predicting Corrosion Rates

Armed with the Tafel equation and Tafel plots, it is now possible to predict whether a particular setup will result in corrosion and if so how fast the corrosion will be.

In order for corrosion to occur, there must be a suitable anodic reaction and an appropriate cathodic reaction. This is manifested as an intersection of a cathodic branch and an anodic branch on a Tafel plot. The point of intersection gives the corrosion potential and the corrosion current (or, more accurately the log of the corrosion current density).

The rate of corrosion is governed by all the factors discussed previously. When all the effects are taken into account, Tafel plots get quite complicated and some interesting effects occur:

Faraday's law allows the current density to be expressed as the mass of material lost per unit time.

The calculation involves a few simple steps. For a corrosion reaction:

The current is converted into a rate of electron consumption using the electronic charge constant. The number of electrons is divided by the stoichiometric number of electrons in the corrosion reaction, giving the number of metal atoms lost per unit time.

This answer is then divided by Avogadro's number to give the number of moles of metal atoms lost per unit time.

The number of moles is then converted to mass lost per unit time, using the molar mass.

The mass is then converted to a volume using the density.

The volume is then converted to a thickness lost per unit time by dividing by the area that the current passes over. If a current density was given, this step has already been done.

Overall, the thickness of metal lost per unit time is given by the formula:

$$t = \frac{im_M}{\rho ezN_A} \quad (9)$$

where

- t thickness (m),
- i current density (A m⁻²),
- m_M molar mass (kg mol⁻¹),
- e electronic charge (C),
- z stoichiometric number of electrons in oxidation reaction,
- N_A Avogadro's number.

It is also possible to have a situation where corrosion does not occur for thermodynamic reasons, for example if there was a driving force for the reverse of the corrosion reaction to occur due to an applied potential. This would result in deposition (electroplating) if there were metal ions in solution available to be reduced. If deposition is being carried out commercially, for example to electroplate silver onto stainless steel cutlery, the rate must be maximized to make production as cost effective as possible. However, care must be taken to avoid the hydrogen evolution reaction starting at the cathode in addition to the metal ion deposition.

Applying an over potential to an electrode drives the reaction in one direction and away from equilibrium. Tafel's law governs the new rate and as long as the reaction kinetics are activation controlled, the over potential is proportional to the log of the corrosion current.

Other factors may limit the maximum rate of corrosion, with oxygen depletion limiting the speed of the cathodic reaction to the rate at which oxygen can be supplied from the bulk. The anodic reaction may be limited by passivation, if a sufficiently large over potential is applied to form a passive layer. Passive layers separate the metal from the electrolyte and slow the corrosion reaction.

Faraday's law can give meaningful results from the predicted corrosion current, i.e. giving the mass loss per unit time.

Corrosion can be slowed by either adding an inhibitor to remove hydrogen ions and move to a passivating region of the Pourbaix diagram, by adding an inhibitor to form a passive layer on the anode, or by adding an inert barrier to the surface of the anode

Linear polarization resistance (LPR)

LPR is most effective in aqueous solutions, and has proven to be a rapid response technique. Electrical conductivity (the reciprocal of resistance) of a fluid can be related to its corrosiveness. The polarization resistance is the ratio of the applied potential and the resulting current level. The measured resistance is inversely related to the corrosion rate. The electrical resistance of any conductor is given by:

$$R = \frac{V}{I} \quad (10)$$

where

- R = Effective instantaneous resistance
- V = Applied voltage
- I = Instantaneous current between electrodes.

If the electrodes are corroding at a high rate with the metal ions passing easily into solution, a small potential applied between the electrodes will produce a high current, and therefore a low polarization Resistance. This corresponds to a high corrosion rate.

Polarization study has been used to investigate the passive film formed on metal surface during corrosion process in presence of inhibitors.⁴⁴⁻⁴⁸ The corrosion parameters of mild steel immersed in an aqueous solution in the absence and presence of inhibitor system are given in Table 2. The corrosion parameters include corrosion potential (E_{corr}), Tafel slopes (b_c = cathodic; b_a =anodic), Linear polarization resistance (LPR) and corrosion current (I_{corr}).

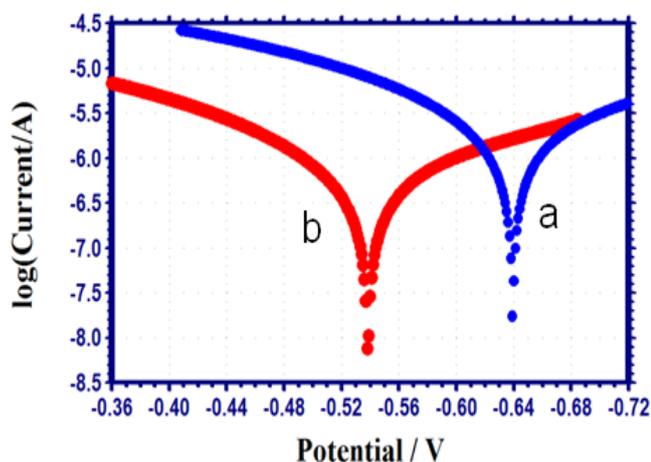


Figure 1. Polarization curve of mild steel immersed in various test solution a) Cl⁻ 60 ppm b) Cl⁻ 60 ppm + glycine 250 ppm + Zn²⁺ 50 ppm

The polarization curves are shown in Figures 1 to 3. When mild steel is immersed in the environment (aqueous solution containing 60 ppm Cl⁻), the corrosion potential is -639 mV vs SCE. The LPR value is 17180 ohmcm² and the corrosion current is 2.241x10⁻⁶A cm⁻². When inhibitor system (glycine 250 ppm + Zn²⁺ 50 ppm) is introduced in the environment; the corrosion potential is shifted to the anodic side that is noble side. This indicates that a passive film is formed on

the metal surface in presence of inhibitor. The shifting of corrosion potential towards anodic side in presence of inhibitors has been reported by several researchers.⁴⁹⁻⁵⁶

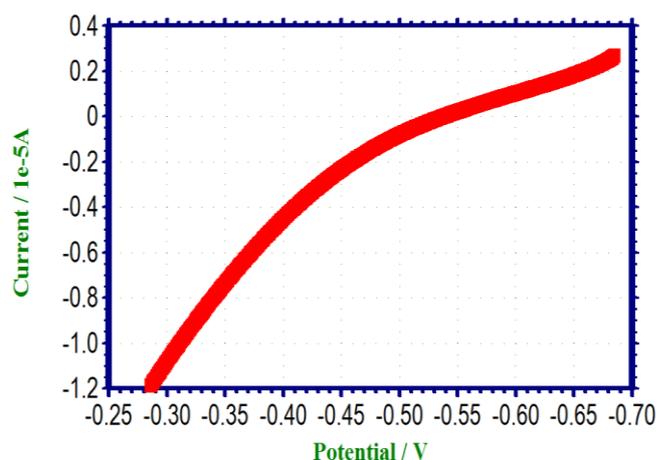


Figure 2. Polarization curve of mild steel immersed in an aqueous solution containing 60 ppm Cl⁻

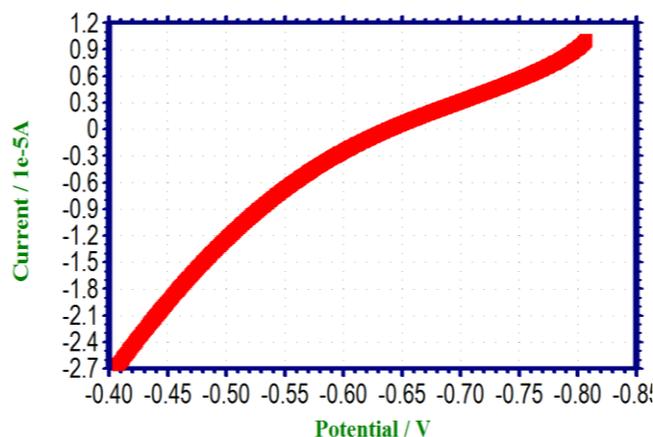


Figure 3. Polarization curve of mild steel immersed in an aqueous solution containing 60 ppm Cl⁻ + glycine 250 ppm + Zn²⁺ 50ppm

Table 2. Corrosion parameters of mild steel immersed in an aqueous solution containing 60 ppm of Cl⁻ obtained from polarization study

System	E_{corr} , mV*	b_a , mV**	b_c , mV**	LPR, ohm cm ²	I_{corr} , A cm ⁻²
Cl ⁻ 60 ppm	-639	202	158	17180	2.241x10 ⁻⁶
Cl ⁻ 60 ppm+A	-538	202	158	53494	6.920x10 ⁻⁷

A = glycine 250 ppm + Zn²⁺ 50 ppm, *mV vs SCE; **mV in one decade

It is also observed that, when inhibitor system is introduced in to the environment, LPR value increases and corrosion current decreases. When a passive film formed on mild steel surface, in presence of inhibitor system, the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So rate of corrosion decreases and hence corrosion current decreases in presence of inhibitor system.

It is observed from Table 2 that the Tafel slope values are not changed much in the presence of inhibitor system, when compared to the blank system. This suggests that the glycine-Zn²⁺ system, controls the anodic reaction



and the cathodic reaction



to an equal system. The anodic reaction is controlled by formation of Fe²⁺-glycine complex on the anodic site of the metal surface. The cathodic reaction is controlled by deposition of Zn(OH)₂ on the cathodic sites of the metal surface. Thus anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect of Zn²⁺- glycine system.^{57, 58}

The variation of current with potential, when mild steel is immersed in blank system and inhibitor system is shown in Figures 3 and 4. It is observed that the rate of change of current with potential is less in presence of inhibitor system than in its absence.

Conclusion

The inhibition efficiency of glycine-Zn²⁺ system has been evaluated by weight loss method and polarization study. Glycine alone has some corrosion inhibition efficiency (IE). In presence of Zn²⁺, IE increases. Synergistic effect exists between Zn²⁺ and glycine. The formulation consisting of 250 ppm of glycine and 50 ppm of Zn²⁺ has 86% IE. Polarization study reveals that this system function as mixed inhibitor system, controlling the anodic reaction and cathodic reaction to an equal extent.

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