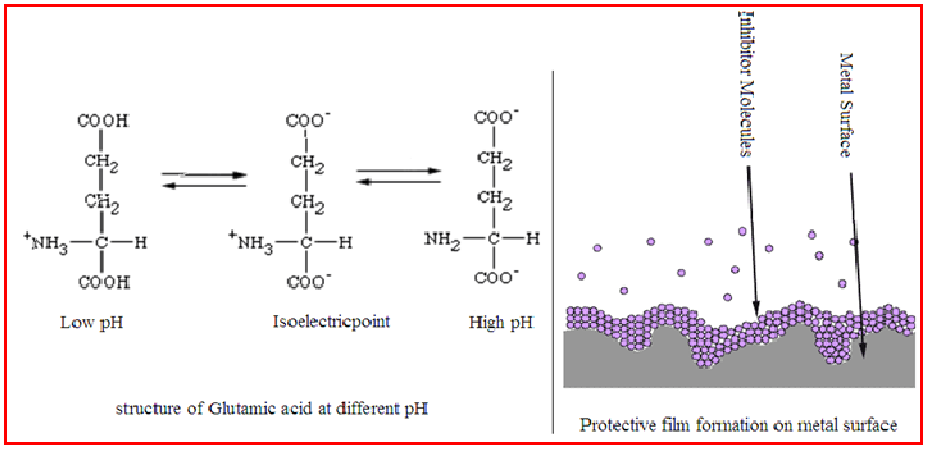
# ELECTROCHEMICAL AND GRAVIMETRIC STUDY ON THE CORROSION AND CORROSION CONTROL OF CARBON STEEL BY THE BINARY FORMULATION CONTAINING L-GLUTAMIC ACID AND ZINC IONS IN AQUEOUS ENVIRONMENT

**[1]Dr.A.Sahaya Raja, Dr.J.Sathiyabama, S.Kannan & [2]Dr.V.Prathipa**

*[1]PG & Research Department of Chemistry, G.T.N. Arts College, Dindigul, Tamilnadu, India*

*[2]Department of Chemistry, PSNA College Engineering and Technology, Dindigul, Tamilnadu, India*

## Graphical Abstract




## Abstract

*The inhibitor system L- Glutamic acid - $Zn^{2+}$ has been investigated by electrochemical and gravimetric (weight loss) techniques at room temperature. At pH-7.6, the formulation consisting of L-Glutamic acid-$Zn^{2+}$ offers 90% inhibition efficiency (IE). Polarization study reveals that this formulation functions as an anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. At isoelectric point (pH-3.1), the IEs of L-Glutamic acid and also the L-Glutamic acid-$Zn^{2+}$ systems are very low. In some cases there is acceleration of corrosion, -33% inhibition efficiency is noticed (negative IEs). The gravimetric measurements aided in the classical prediction of the corrosion inhibition process.*

***Keywords:*** *Corrosion, Carbon steel, L- Glutamic acid, $ZnSO_4$, Gravimetric Technique, Polarization study, AC impedance spectra*

## Introduction

Carbon steel finds a lot of application in industries particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. It gets rusted when it comes in contact with any aqueous medium. Corrosion is the deterioration of metal by chemical or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. The use of inhibitors is one of the best methods for protecting metals against corrosion. Inhibitors are substance which when added in small quantity to a corrosive environment, lower the corrosion rate. They reduce the corrosion by either acting as a barrier, by forming an adsorbed layer or retarding the cathodic and /or anodic process. The majority of well –known inhibitors are organic compounds containing heteroatom, such as O, N, S and multiple bonds [1]. Most of the organic compounds are not only expensive but also toxic to both human beings and environments [2] and therefore the use of hazardous chemical inhibitors is totally reduced because of environmental regulations. It is

better to look for environmentally safe inhibitors. Many researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion [3-13]. This is due to the fact that amino acids are non-toxic, biodegradable, relatively cheap, and completely soluble in aqueous media and produced with high purity at low cost. Various amino acids have been used to inhibit the corrosion of metals and alloys [14-17]. Perusal of several literatures reveals that there is no information regarding the use of L-Glutamic acid in combination with Zinc ion ($Zn^{2+}$). Therefore, environmental friendly inhibitor L-Glutamic acid is chosen as the corrosion inhibitor for this present work. The aim of this research is to investigate the inhibition efficiency of L-Glutamic acid in controlling the corrosion of carbon steel in the absence and presence of $Zn^{2+}$ at pH – 7.6 and isoelectric point (pH – 3.1). The investigation is performed using gravimetric (weight loss) technique, electrochemical studies such as polarization and AC – impedance spectroscopy.

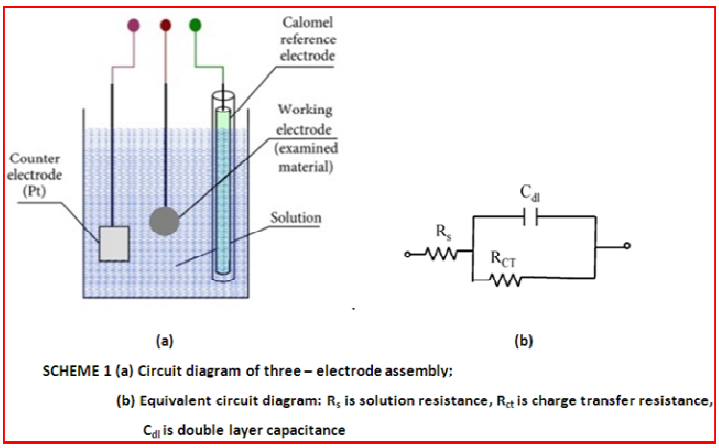
## Material and Methods

### Gravimetric Measurements

All the weight of the carbon steel specimens before and after corrosion was carried out using Shimadzu Balance-AY62. Inhibition efficiency (IE) was calculated from the relationship $IE = 100\ [1 - (W_2/W_1)]$, where $W_1$ is the corrosion rate in the absence of inhibitor and $W_2$ is the corrosion rate in the presence of inhibitor.

### Electrochemical and Impedance Measurements

Potentiodynamic polarization studies and AC Impedance measurements are carried out using CHI electrochemical impedance analyzer (model 660A) is shown in scheme 1. All solutions were prepared using well water collected from G.T.N. Arts College, Dindigul, Tamil Nadu, India. The study was carried out at room temperature (303K). The chosen environmental well water and its some physicochemical parameters are pH- 7.6,Conductivity - 1870 µmhos/cm,TDS – 1329ppm,TH – 700ppm, Chloride – 727ppm.




SCHEME 1 (a) Circuit diagram of three – electrode assembly;
(b) Equivalent circuit diagram: $R_s$ is solution resistance, $R_{ct}$ is charge transfer resistance, $C_{dl}$ is double layer capacitance

## Result and Discussion

### Analysis of the Gravimetric (Weight Loss) Measurements

Inhibition efficiencies (IEs) of carbon steel immersed in well water in the absence and presence of inhibitor (L-Glutamic acid) are shown in Fig.1. It is observed that L - Glutamic acid shows some inhibition efficiencies. 50 ppm of L - Glutamic acid has 35 percent IE, as the concentration of L - Glutamic acid increases the IE decreases. This is due to the fact that as the concentration of L-Glutamic acid increases, the protective film (probably iron -

L-Glutamic acid complex) formed on the metal surface goes into solution. That is, the system passes from passive region to active region. The influence of $Zn^{2+}$, the concentration of L- Glutamic acid increases the IE increases.

It is also observed that a synergistic effect exists between L - Glutamic acid and $Zn^{2+}$. For example, 5 ppm of $Zn^{2+}$ has 15 percent IE; 250 ppm of L - Glutamic acid has 7 percent IE. Interestingly their combination has a high IE, namely, 90 percent. In presence of $Zn^{2+}$ more amount of L - Glutamic acid is transported towards the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between $Zn^{2+}$ and L-Glutamic acid.

The IE of L-Glutamic acid -$Zn^{2+}$ system at the isoelectric point of L - Glutamic acid (pH=3.1) is shown in Fig.1, the IEs of L-Glutamic acid and also the L-Glutamic acid-$Zn^{2+}$ systems are very low. In some cases there is acceleration of corrosion (negative IEs).

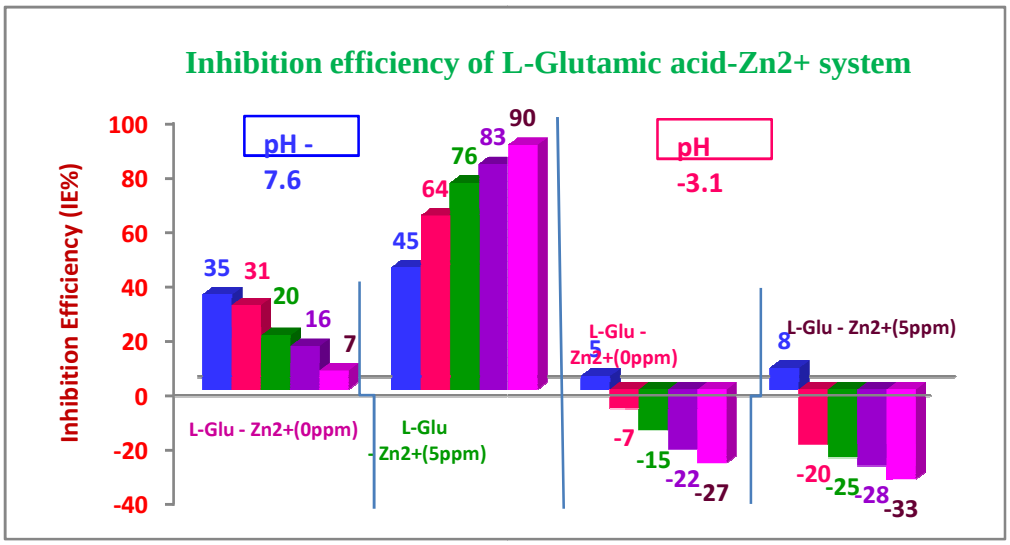



**Fig.1 Inhibition Efficiencies (IEs) of L-Glutamic Acid -$Zn^{2+}$ System Obtained by Gravimetric (Weight Loss) Method**

**Analysis of Potentiodynamic Polarization Study**

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [18-20]. If a protective film is formed on the metal surface, the corrosion current value ($I_{corr}$) decreases. The potentiodynamic 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 1. When carbon steel was immersed in well water the corrosion potential was -675 mV vs SCE. When L - Glutamic acid (250 ppm ) and $Zn^{2+}$ (5 ppm) were added to the above system the corrosion potential shifted to the noble side -628 mV vs SCE. This indicates that a protective film is formed on the anodic sites of the metal surface. Further the corrosion current decreases from $5.793 \times 10^{-7}$ A/cm$^2$ to $4.977 \times 10^{-7}$ A/cm$^2$ Thus polarization study confirms the formation of a protective film on the metal surface.

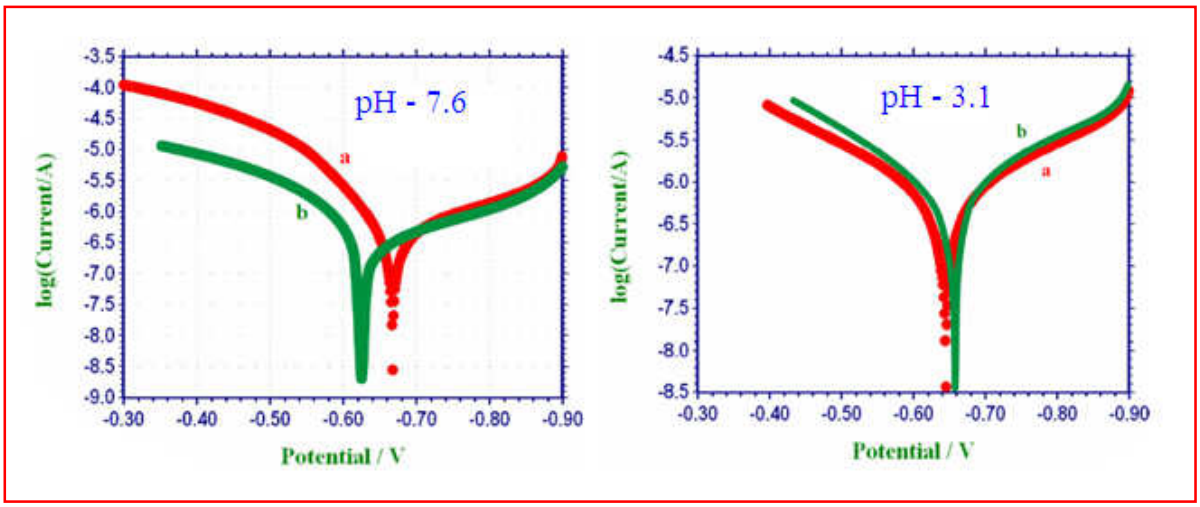
At isoelectric point, when carbon steel was immersed in well water the corrosion potential was -642 mV vs SCE. When L-Glutamic acid(250 ppm) and $Zn^{2+}$ (5 ppm) were added to the

above system, the corrosion potential shifted to -658 mV vs SCE. The corrosion potential is shifted cathodic side (active site). It is observed that $I_{corr}$ value increases, there is no protection of metal and the metal undergoes corrosion. This is in agreement with weight loss results.

**Table 1 Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study**

| System | At pH – 7.6 | | At pH – 3.1 | |
|---|---|---|---|---|
| | Tafel Results | | Tafel Results | |
| | $E_{corr}$ mV vs SCE | $I_{corr}$ A/cm² | $E_{corr}$ mV vs SCE | $I_{corr}$ A/cm² |
| Well water | -675 | 5.793 X $10^{-7}$ | -642 | 6.422 X $10^{-7}$ |
| Well water +L - Glutamic acid(250ppm)+ $Zn^{2+}$ (5ppm) | -628 | 4.977 X$10^{-7}$ | -658 | 6.830 X$10^{-7}$ |

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




**a) Well water (Blank); b) Well water + L - Glutamic acid (250 ppm) + $Zn^{2+}$ (5 ppm)**

**Analysis of AC Impedance spectra**

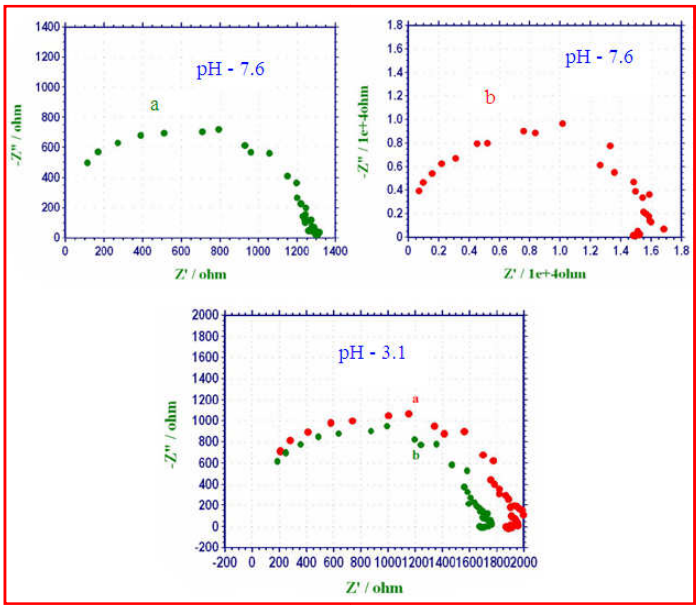
AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface [21-22]. If a protective film is formed on the metal surface, charge transfer resistance ($R_t$) increases; double layer capacitance value ($C_{dl}$) decreases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L - Glutamic acid - $Zn^{2+}$) are shown in Fig-3 (Nyquist plot). The AC impedance parameters namely charge transfer resistance ($R_t$) and double layer capacitance ($C_{dl}$) derived from Nyquist plot are given in Table 2. It is observed that when the inhibitors (L - Glutamic acid (250 ppm) +$Zn^{2+}$ (5 ppm)) are added the charge transfer resistance ($R_t$) increases from 1288 Ω cm² to 16352 Ω cm². The $C_{dl}$ value decreases from 3.6473x$10^{-9}$ F/cm² to 3.2960x$10^{-10}$ F/cm². These results lead to the conclusion that a protective film is formed on the metal surface.

At isoelectric point, when the inhibitors [L-Glutamic acid (250 ppm) + $Zn^{2+}$ (5 ppm)] are added, the charge transfer resistance ($R_t$) decreases from 1550 Ω $cm^2$ to 1480 Ω $cm^2$. The $C_{dl}$ value increases from 3.3035 x$10^{-9}$ F/$cm^{-2}$ to 3.4759 x$10^{-9}$ F/$cm^{-2}$. When a protective film is not formed, charge transfer resistance ($R_t$) decreases and $C_{dl}$ increases; the impedance value decreases, there is no protection of metal, the metal undergoes corrosion. This is in agreement with weight loss results.

**Table 2 Corrosion Parameters of Carbon Steel Immersed in Well Water in the Absence and Presence of Inhibitor System Obtained from AC Impedance Spectra**

| System | At pH – 7.6 | | At pH – 3.1 | |
|---|---|---|---|---|
| | Nyquist plot | | Nyquist plot | |
| | $R_t$ Ω $cm^2$ | $C_{dl}$ F/$cm^2$ | $R_t$ Ω $cm^2$ | $C_{dl}$ F/$cm^2$ |
| Well water | 1288 | 3.6473x$10^{-9}$ | 1550 | 3.3035 x$10^{-9}$ |
| Well water + L - Glutamic acid(250ppm)+ $Zn^{2+}$ (5ppm) | 16352 | 3.2960x$10^{-10}$ | 1480 | 3.4759 x$10^{-9}$ |

**Fig.3 AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots)**




**a) Well water (Blank) ; b)Well water + L - Glutamic acid(250 ppm) + $Zn^{2+}$ (5 ppm)**

**Conclusion**

The results of the gravimetric (weight loss) study show that the formulation consisting of 250 ppm L-Glutamic acid, 5 ppm of $Zn^{2+}$ has 90% IE, in controlling corrosion of carbon steel in well water. A synergistic effect exists between $Zn^{2+}$ and L-Glutamic acid system. Polarization study reveals that the formulation functions as anodic inhibitor controlling the anodic reaction

predominantly and to some extent controls the cathodic reaction. AC impedance spectra reveal that a protective film is formed on the metal surface. At isoelectric point (pH=3.1), L-Glutamic acid exists as zwitter ion. At isoelectric point, when an electric field is applied there is no movement of ions, the IEs of L-Glutamic acid and also the L-Glutamic acid-$Zn^{2+}$ systems are very low. In some cases there is acceleration of corrosion, -33% inhibition efficiency is noticed (negative IEs). Polarization study and AC impedance spectra revealed that there is no synergistic effect exists between $Zn^{2+}$ and L-Glutamic acid and indicated that there is no protection of metal, the metal undergoes corrosion. This is due to the fact that at isoelelctric point there is no migration of L-Glutamic acid towards the metal surface. Therefore amount of L-Glutamic acid transported towards the metal surface is reduced. So, metal is not protected by L-Glutamic acid. Hence there is no IE at isoelectric point.

**Acknowledgement**

The authors are thankful to their respective management, Principal, G.T.N.Arts College, Dindigul, Tamil Nadu, and India for providing the required facilities for completion of the work.

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