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Corrosion inhibition by monosodium glutamate-Zn^{2+} system

The inhibition efficiency of mono sodium glutamate (MSG)-Zn^{2+} system in controlling corrosion of carbon steel in an aqueous environment has been evaluated by mass- loss method. The synergistic effect is noticed between mono sodium glutamate and Zn^{2+}. The formulation consisting of 100 ppm of mono sodium glutamate and 50 ppm of Zn^{2+} shows 86% inhibition efficiency(IE).At lower pH value IE decreases and in alkaline solution IE increases. Polarisation study reveals that MSG-Zn^{2+} system functions as a mixed inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+}-MSG complex and $Zn(OH)_2$.

INTRODUCTION

The use of inhibitors is one of the most practical methods to protect metals from corrosion. During the past decade, the inhibition of copper in hydrochloric acid by different types of organic inhibitors has been extensively studied [1-7]. Unfortunately, many common corrosion inhibitors are highly toxic and health-hazardable, such as chromates [8], nitrite [9], and aromatic heterocyclic compounds [10] etc. Their replacement by new environment-friendly inhibitors is desirable. Some researchers investigated the inhibition effect of environment-friendly inhibitors such as amino acids on metal corrosion [11-18]. Amino acids are nontoxic, biodegradable, relatively cheap and completely soluble in aqueous media. The number of publications on the inhibition effect of some amino acids on corrosion of metals increases. El-Shafei [19] studied the effect of six α-amino acids for pitting corrosion of aluminum in chloride media.

Da-Quan Zhang et al., [20] investigated the inhibition properties of four aminoacids aspartic acid (Asp), glutamic acid (Glu), asparagine (Asn), glutamine (Gln)) on copper corrosion in 0.5M HCl solution. Aspartic acid and glutamic acid are attarctive due to the presence of two carboxyl groups. Molecular modification can be done by the acylamidation of these carboxyl groups. Bereket and Yurt [21] have studied the inhibition effect of amino acids and hydroxy carboxylic acids on pitting corrosion of Al alloy in NaCl solution at various pH levels by potentiostatic methods. Amino acids shift the E_{pit} values to noble direction in acidic solutions, while hydroxy carboxylic acids are effective in neutral and basic solutions. According to Pech and Bartolo [22] the inhibitive effect of N-phosphonomethyl glycine-Zn^{2+} mixture on corrosion of steel in neutral medium is due to the retardation of anodic and cathodic processes due to the film, Fe- inhibitor complex and ZnO. Zerfaoui et al[23] have reported the corrosion behavior of pure iron in citric acid in the presence of glycine, leucine, aspartic acid, arginine, and methionine and they were found to act as cathodic inhibitors.

The present work is undertaken: (i) to evaluate the inhibition efficiency of mono sodium glutamate (MSG) in controlling corrosion of carbon steel in river (namely, The Cauvery in Trichy, Tamilnadu, India) water (Table 1), in the presence and absence of Zn^{2+} (ii) to analyse the protective film by FTIR (iii) to know the mechanistic aspects of corrosion inhibition by polarization study and AC impedance spectra (iv) to study the formation of metal complexes in solution by UV absorption spectral studies and (v) to propose a suitable mechanism based on the results from the above studies.

EXPERIMENTAL

Preparation of the carbon steel specimens

Carbon steel specimens (0.026 % S, 0.06 % P, 0.40 % Mn, 0.10 % C, and the rest iron) of dimensions 1.0 × 4.0 × 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass loss and surface examination studies.

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Table 1: Results of the analysis of the sample of river (Cauvery) water

S.No	Chemical Examination	Acceptable limit	Test Results
1	pH	7.0 - 8.5	7.1
4	Total Hardness (ppm)	200 - 600	106
5	Ca(ppm)	150 - 200	21
6	Mg(ppm)	50 - 150	23
7	Fe(ppm)	20	0.62
8	Mn(ppm)	0.5	0.03
10	Nitrite as NO_2 (ppm)	--	0.01
11	Nitrate as NO_3(ppm)	20	0.05
12	Chloride as Cl(ppm)	200 - 600	254
13	Fluoride as F^-(ppm)	1	0.2
14	Sulphate as SO_4(ppm)	42 - 45	0.08
15	P (ppm)	5	0.1
16	Total dissolved solids (mg/l)	500 - 1500	153

Mass- loss method

The weighed specimens in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions. After 3 days of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimens, corrosion rates and I.E. were calculated.

$$IE = 100 [1 - (W_2 / W_1)] \%$$

Where W_1 = corrosion rate (mdd) in absence of inhibitor, W_2 = corrosion rate (mdd) in presence of inhibitor.

Surface examination studies

The carbon steel specimens were immersed in various test solutions for a period of three days, the specimens were taken out, washed with distilled water and then dried. The nature of the film formed on the surface of metal specimens was analysed by the following techniques.

FTIR spectra

The film was carefully removed with sharp edged glass rod, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded on a Perkin- Elmer 1600 spectrophotometer.

Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out using CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm^2 area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance measurements

A CHI electrochemical impedance analyzer (model 660 A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open-circuit potential. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies (f). The values of the charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

The UV-visible absorption spectra of solutions

The possibility of the formation of Zn- inhibitor complex and also iron-inhibitor complex in solution was examined by mixing the respective solutions and recording their UV-visible absorption spectra using Lamda 35 UV-visible spectrophotometer 119 which is a PC controlled single beam scanning spectrophotometer. It covers a wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1nm.

RESULTS AND DISCUSSION

Mass loss method

The corrosion inhibition efficiencies of mono sodium glutamate (MSG)-Zn^{2+} systems, as determined by mass loss method, are given in Table 2. It is found from the table that MSG is a poor inhibitor and 100 ppm of MSG gives a maximum of 36 % IE. Perusal of the table reveals that a combination of Zn^{2+} and MSG shows a better IE. For example, 50 ppm of Zn^{2+} gives an IE of 41 % and 100 ppm of MSG gives 36 %, but their combination offers an IE of 86 %, which is found to be the maximum IE offered by the system. This suggests the existence of synergistic effect between Zn^{2+} and MSG. The synergism may be due to the formation of complex between Zn^{2+} and MSG. Because of the complex formation with Zn^{2+} the inhibitor molecules are readily transported from the bulk to the metal surface.

On the metal surface, Zn^{2+}-MSG complex is converted into Fe^{2+}- MSG complex on the anodic sites of the metal surface. Zn^{2+} is released. This combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus both the anodic reaction

$$Fe \text{---------}> Fe^{2+} + 2e^-$$

cathodic reaction

$$O_2 + 4e^- + 2H_2O \text{---------}> 4OH^-$$

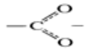
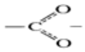
are controlled effectively.. This accounts for a synergistic effect between MSG and Zn^{2+}.

Table 2: Inhibition efficiency (%) of MSG-Zn^{2+} system on the corrosion of carbon steel in river (The Cauvery) water.

Immersion period: 3 days

MSG ppm	Zn^{2+},ppm				
	0	5	10	25	50
0	--	20	33	39	41
10	8	30	61	55	66
25	14	34	58	63	72
50	21	24	55	68	76
75	29	30	47	71	79
100	36	45	47	76	86
125	30	44	51	72	73

FTIR spectral analysis

The FTIR spectrum of MSG (Fig. 3a) shows a series of bands from 3412 cm^{-1} to 2627 cm^{-1}. This is due to the NH_3^+ stretching band and multiple combination and overtone bands of NH_3^+ group. There is a band at 1686 cm^{-1} due to a weak asymmetrical bending band of NH_3^+. The bands at 1606.4 cm^{-1} and 1399.1 cm^{-1} are due to the carboxylate anion  The band at 528.84 cm^{-1} is due to the tortional oscillation of the NH_3^+. The FTIR spectrum of thin film (Fig.3b) shows a band at 3427.33 cm^{-1} the disappearance of the shoulder peaks in the thin film clearly indicates the absence of zwitter ion which clearly shows the absence of OH group which in turn indicates the involvement of O- and amino group in the complex formation. The bands at 1606.4 cm^{-1} and 1399.1 cm^{-1} are due to  group in the *i*R spectrum of MSG is shifted to 1602 cm^{-1} and 1415 cm^{-1} in the *i*R spectrum of the thin film which shows that the carboxylate ion is involved in complex formation. The disappearance of band at 1686 cm^{-1} due to asymmetric bending band and a band at 528 cm^{-1} due to tortional oscillation of the quaternary ammonium ion also proves that nitrogen atom is also involved in complex formation. The presence of bands at 3770 cm^{-1} (M-OH stretching) [24], 1359 cm^{-1} (OH inplane bending) [25] and 772 cm^{-1} (M-O bond) clearly shows the formation of metal hydroxide [26].

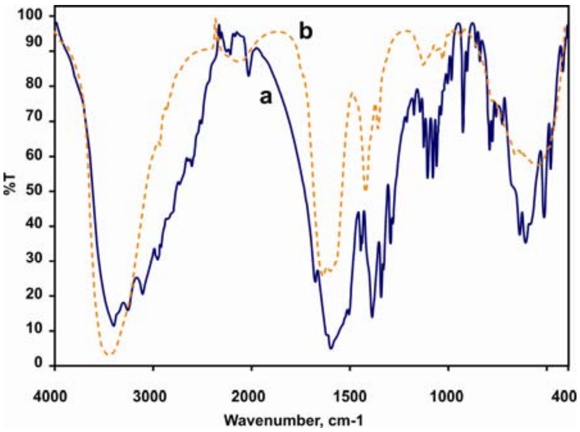


Fig. 1: FTIR spectra of a) MSG and b) Film formed on steel after immersion in river water containing 100 ppm MSG and 50 ppm Zn^{2+}.

Analysis of the results of potentiodynamic polarization studies

The corrosion parameters of carbon steel immersed in river (The Cauvery) water in the presence and absence of 50 ppm of Zn^{2+} and 100 ppm of MSG are given in Table 3.

***Table 3** - Corrosion parameters of carbon steel in river water(Cauvery) in the presence and absence of inhibitor obtained by potentiodynamic polarization*

Environment	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR Ω cm^2	I_{corr} A/cm^2
River water	-463	327	217	3.643×10^3	1.556×10^{-5}
River water + 100 ppm MSG + 50 ppm Zn^{2+}	-357	276	226	5.162×10^3	1.048×10^{-5}

When carbon steel is immersed in river water, the corrosion potential (E_{corr}) is -463 mV vs SCE and the corrosion current is 1.556×10^{-5} A/cm^2. When 50 ppm of $Zn^{2+}$and 300 ppm of mono sodium glutamate are added to river water the corrosion potential shifts to the anodic side -357 mV vs SCE. The corrosion current is 1.048×10^{-5} A/cm^2. The cathodic slope is found to change from 327 to 276 mV/ decade and the anodic slope from 217 to 226 mV/ decade. The linear polarization resistance has increased from 3.643×10^3 to 5.162×10^3 Ωcm^2. The increase in the value of b_c is considerably more than that of b_a. This shows that the formulation controls the cathodic reaction predominantly.The increase in LPR value and decrease in corrosion current indicate that a protective film is formed on the metal surface [27].

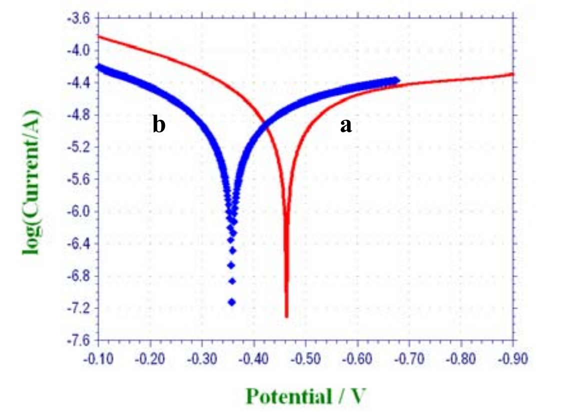


Fig.2 - Polarization curves of carbon steel immersed in various test solution: a) River water (RW), b) RW containing 100 ppm MSG and 50 ppm Zn^{2+}

Analysis of the results of AC impedance studies

The AC impedance spectra of carbon steel immersed in various test solutions are shown in Fig.3.

The AC impedance parameters namely charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) are given in Table 4.

When carbon steel is immersed in river water the R_t value is found to be 1102 Ω cm^2. The C_{dl} value is 8.2187×10^{-9} F/cm^2. When 50 ppm of $Zn^{2+}$and 300 ppm of mono sodium glutamate are added the R_t value has increased from 1102 to 1622 Ωcm^2 and the C_{dl} value has decreased from 8.2187×10^{-9} to 5.8861×10^{-9} F/cm^2. The increase in R_t values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in river water. This behaviour means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film [28].

Table 4: Impedance parameters of carbon steel in river water in the absence and presence of inhibitor obtained by AC impedance spectra

Environment	**R_t Ω cm^2**	**C_{dl} F/cm^2**
River water	1102	8.2187×10^{-9}
River water +100 ppm MSG + 50 ppm Zn^{2+}	1622	5.8861×10^{-9}

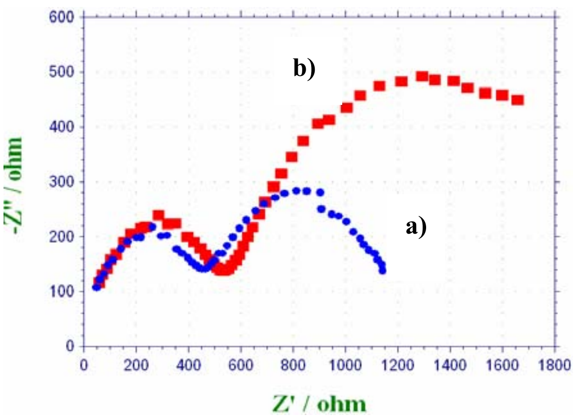
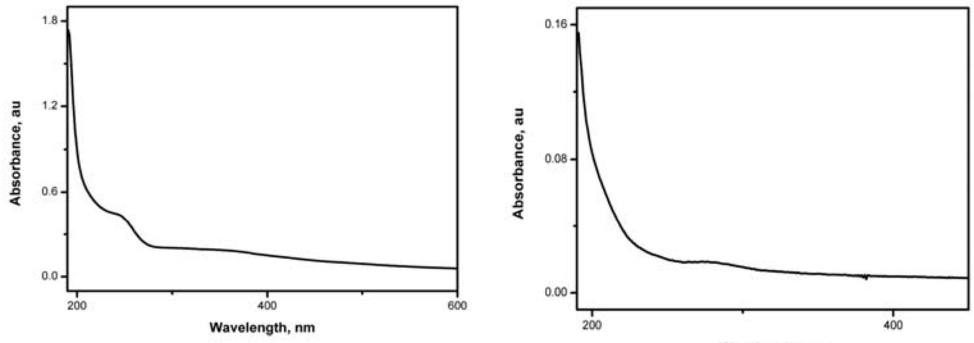


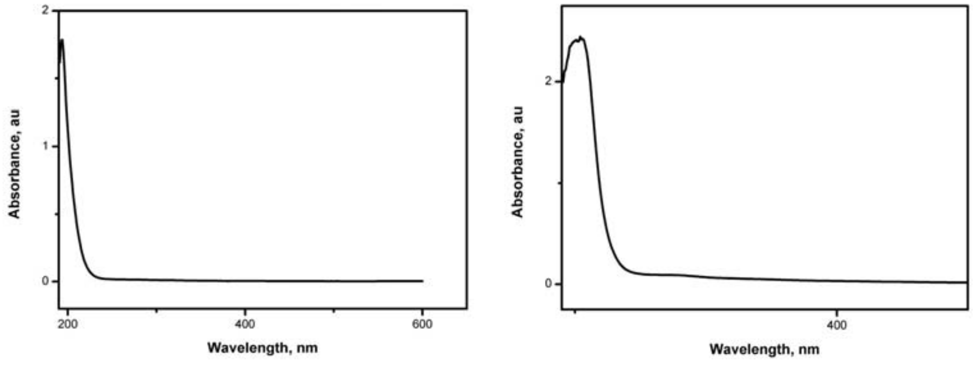
Fig.3 - AC impedance spectra of carbon steel immersed in various test solutions: a) River water, b) River water + 100 ppm MSG + 50 ppm Zn^{2+}

UV-Visible spectral study

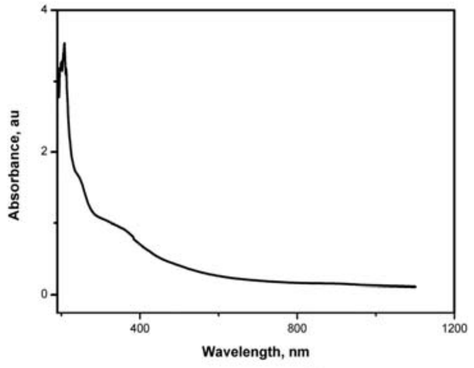
The UV-visible spectrum of Zn^{2+}, Fe^{2+} ion, MSG, Zn^{2+}-MSG and Fe^{2+}- MSG in distilled water are given in Figs. 4a-e. The UV spectrum of MSG (Fig.4c) shows a peak at 193.61 nm with the absorbance value of 1.7918. Addition of Zn^{2+} ion shifts this peak to 204.05 nm with the absorbance value of 2.4453(Fig.4d). When Fe^{2+} is added to SG solution an new peak appears at 196.26 nm with increased intensity (abs 3.204). This shows that MSG readily forms complexes with both Fe^{2+} and Zn^{2+} ions.



(a) Zn^{2+} ions **(b) Fe^{2+} ions**



(c) MSG **(d) MSG and Zn^{2+} ions**



(e) MSG and Fe^{2+} ions

Fig - 4 - UV-Visible absorption spectra of the test solutions in river water

Mechanism of corrosion inhibition:

- The analysis of the results of the mass-loss method shows that the formulation consisting of 100 ppm of mono sodium glutamate and 50 ppm of Zn^{2+} offers maximum IE of 86%.
- The AC impedance spectral studies reveal the formation of a film with higher resistance than that of the river water alone.
- Results of polarization study show that this formulation functions as a mixed inhibitor but more predominantly controlling cathodic process.
- The UV – visible absorption spectra indicate the possibility of formation of iron- MSG complex and also Zn^{2+} - MSG complex in solution.
- The FTIR spectra confirm the formation of film consisting of iron - MSG complex and $Zn(OH)_2$.

Based on the above facts the following mechanism is proposed

- In river (The Cauvery) water containing 50 ppm of Zn^{2+} and 100 ppm of mono sodium glutamate, a sort of complex is formed between Zn^{2+} and mono sodium glutamate.
- When the metal is immersed in this environment, this complex diffuses from the bulk of the solution to the surface of the metal.
- On the surface of the metal, Zn complex is converted into the iron complex at the local anodic sites, as the latter is more stable than the former.
- Zn-Complex + Iron $\rightarrow$ Iron – Complex + Zn^{2+}.
- The released Zn^{2+} ions will form Zn $(OH)_2$ in the local cathodic regions.
- The protective film consists of iron-complex and $Zn(OH)_2$ [29,30].

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