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Experimental study of inhibition effect, synergistic effect and antagonistic behaviour of L-phenylalanine – $ZnSO_4$ at pH – 7.2 and isoelectric point (pH – 5.9) on carbon steel in aqueous solution

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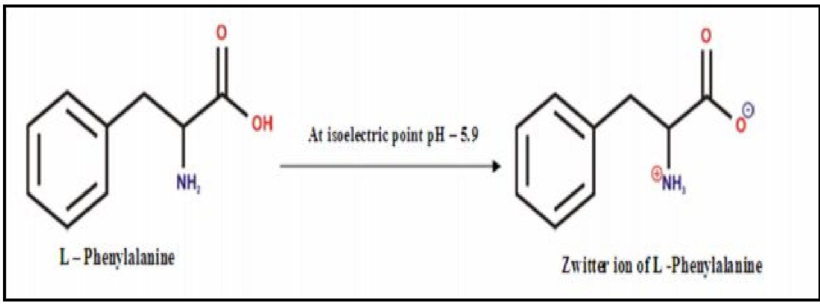
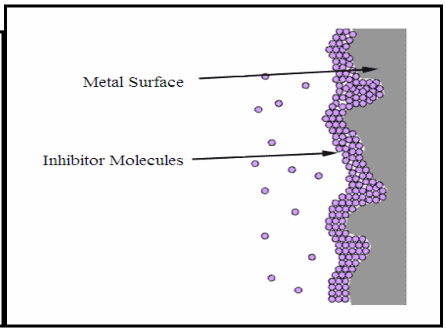
Abstract: The inhibition and antagonistic effects of L – Phenylalanine on the corrosion of carbon steel in well water have been studied using weight loss method, Polarization study and AC impedance spectra. A synergistic effect exists between L – Phenylalanine and Zn^{2+} system. The formulation consisting of L – Phenylalanine - Zn^{2+} offers good inhibition efficiency. 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. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study and electrochemical studies. At isoelectric point there is no migration of L – Phenylalanine towards the metal surface. Therefore amount of L – Phenylalanine transported towards the metal surface is reduced. So, metal is not protected by L – Phenylalanine. Hence there is no IE at isoelectric point.
Keywords: Carbon steel, L – Phenylalanine, ZnSO4, Polarization study, AC impedance spectra, antagonistic effect, synergistic effect, isoelectric point.

Graphical Abstract



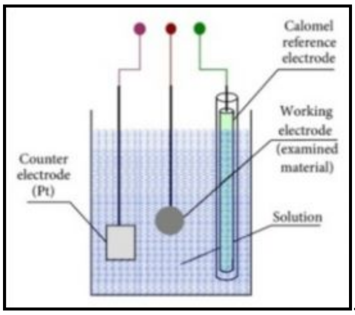


Introduction

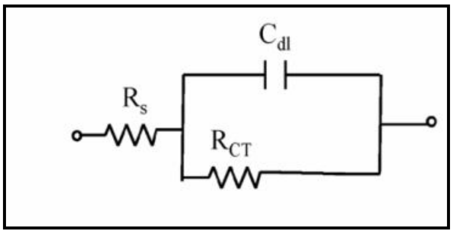
A corrosion inhibitor is a substance when added in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment. Inhibitors often play an important role in the oil extraction and processing industries where they have always been considered to be the first line of defence against corrosion[1]. Among the various methods to avoid or prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best know methods of corrosion protection and one of the most useful on the industry. This method is following stand up due to low cost and practice method[2-3].Historically, inhibitors had great acceptance in the industries due to excellent anti-corrosive proprieties. However, many showed up as a secondary effect, damage the environment. Thus the scientific community began searching for friendly environmentally inhibitors, like the organic inhibitors[4-5] and amino acids[6-8]. Various amino acids have been used to inhibit the corrosion of metals and alloys[9-17]. Synergistic and Antagonistic Effect of L – Alanine for carbon steel in aqueous medium has been investigated[9]. Eco–Friendly Inhibitor L–Cysteine–Zn^{2+} System to control corrosion of carbon steel in aqueous medium was analyzed[10]. Prathipa et al was studied corrosion inhibition of carbon steel using green inhibitor (L-Alanine)[11]. Sivakumar et al have used L-Histidine to prevent corrosion on carbon steel[12].Amino acid such as DL-Phenylalanine has been used to prevent corrosion of carbon steel[13]. Sahaya Raja et al have used L - Phenylalanine along with Zn^{2+} to prevent corrosion of carbon steel in well water[14]. Arginine - Zn^{2+} system has been used to inhibit corrosion of carbon steel[15-16]. L – Alanine as inhibitor for carbon steel in well water was studied[17]. The environmental friendly amino acid such as L – Phenylalanine is chosen as the corrosion inhibitor for this present work. The aim of this research is to investigate the Inhibition, Synergistic and Antagonistic Effect of L -Phenyalanine. For this purpose the electrochemical studies such as potentiodynamic polarization and AC impedance spectroscopy have been used in the present study.

2. Materials and Methods

Determination of corrosion rate - All the weight of the carbon steel specimens before and after corrosion was carried out using Shimadzu Balance-AY62.Corrosion rates were calculated using the following relationship. Corrosion Rate (mm/y) = [loss in weight (mg) X 1000 / surface area of the specimen (dm^2) X period of the immersion (days)] X (0.0365/ ρ).**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 & 2.**



SCHEME – 1: Circuit diagram of three – electrode assembly



SCHEME -2: Equivalent circuit diagram:
R_s is solution resistance,
R_{ct} is charge transfer resistance,
C_{dl} is double layer capacitance

3. Results and discussion

3.1Analysis of the weight loss method

Corrosion rates (CR) of carbon steel immersed in well water in the absence and presence of inhibitor (L -Phenylalanine) are given in **Table.1** the inhibition efficiencies (IEs) are also given this table. It is observed from **Table.1**, that L –phenylalanine shows some inhibition efficiencies. 50 ppm of L - Phenylalanine has 20 percent IE, as the concentration of L - Phenylalanine increases, IE increases.

3.2 . Synergism and Antagonism

The influence of Zn^{2+} on the inhibition efficiencies of L - Phenylalanine is given in **Table.1** and shown in the **Figure.1.** It is observed that as the concentration of L - Phenylalanine increases the IE increases. Similarly, for a given concentration of L - Phenylalanine the IE increases as the concentration of Zn^{2+} increases. It is also observed that a synergistic effect exists between L - Phenylalanine and Zn^{2+}. For example, 5 ppm of Zn^{2+} has 10 percent IE; 250 ppm of L - Phenylalanine has 35 percent IE. Interestingly their combination has a high IE, namely, 95 percent. In presence of Zn^{2+} more amount of L - Phenylalanine is transported towards the metal surface. On the metal surface Fe^{2+}- L - Phenylalanine complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH^-, which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of 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 - Phenylalanine.

$Fe \dashrightarrow Fe^{2+} + 2e^-$ (Anodic reaction)
$Fe^{2+} + Zn^{2+}$- L-Phenylalanine complex $\dashrightarrow Fe^{2+}$-L-Phenylalanine complex + Zn^{2+}
$O_2 + 2H_2O + 4e^- \dashrightarrow 4OH^-$ (Cathodic reaction)
$Zn^{2+} + 2OH^- \dashrightarrow Zn(OH)_2 \downarrow$

3.2.1. Synergism parameters (S_I)

The synergism parameters (S_I) of L - Phenylalanine-Zn^{2+} system were found to be one and above (S_I>1, it points to synergistic effects) [13-17]. This indicates that the synergistic effect exist between L - Phenylalanine and Zn^{2+}.

3.2.2. Antagonism

The IE of L - Phenylalanine -Zn^{2+} system at the isoelectric point of L - Phenylalanine (pH=5.9) is given in **Table.1** and shown in the **Figure.1**. At isoelectric point, L - Phenylalanine exists as zwitter ion, when an electric field is applied there is no movement of ions[9,18].Accordingly it is observed from **Table.1** the IEs of L - Phenylalanine and also the L - Phenylalanine -Zn^{2+} systems are very low. In some cases there is acceleration of corrosion (negative IEs).

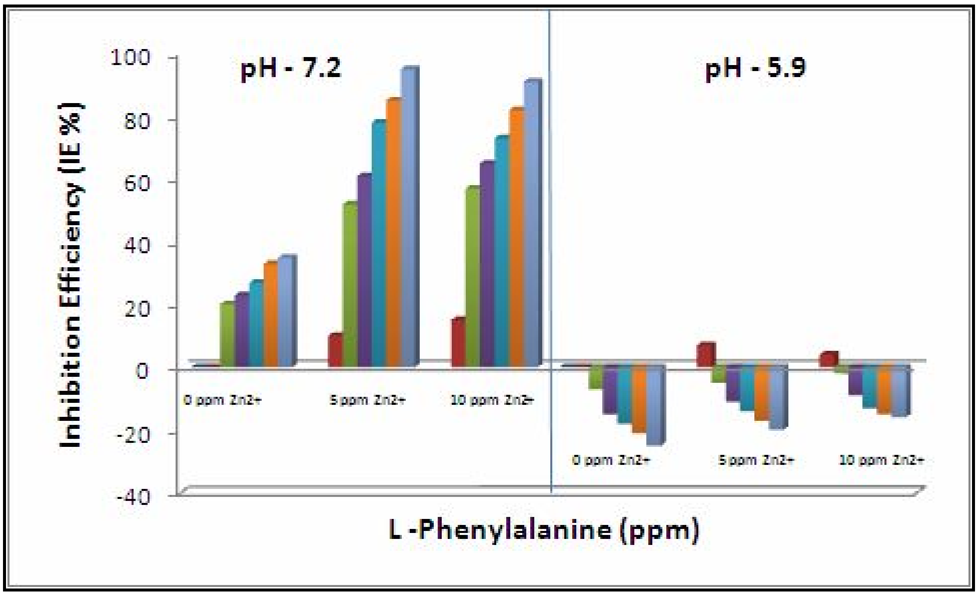


Figure – 1: The presence and absence of inhibitor system at various concentrations and the inhibition efficiencies at pH – 7.2 and pH – 5.9

Table.1: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IEs) obtained by weight loss method.

Inhibition system : L - Phenylalanine - Zn^{2+} (0 ppm and 5ppm), Immersion period : 1 day

Inhibitor Environment	L – Phenylalanine (ppm)	Zn^{2+} ion					
		0 ppm		5 ppm		10 ppm	
		IE %	CR (mm/y)	IE %	CR (mm/y)	IE %	CR (mm/y)
L – Phenylalanine at pH – 7.2	0	-	0.0490	10	0.0441	15	0.0417
	50	20	0.0392	52	0.0235	57	0.0210
	100	23	0.0377	61	0.0191	65	0.0171
	150	27	0.0358	78	0.0107	73	0.0132
	200	33	0.0328	85	0.0073	82	0.0088
	250	35	0.0318	95	0.0024	91	0.0044
L – Phenylalanine at pH – 5.9	0	-	0.0700	7	0.0651	4	0.0672
	50	-7	0.0750	-5	0.0735	-2	0.0714
	100	-15	0.0806	-11	0.0778	-9	0.0764
	150	-18	0.0827	-14	0.0799	-13	0.0792
	200	-21	0.0848	-17	0.0820	-15	0.0806
	250	-25	0.0876	-20	0.0841	-16	0.0813

4. Analysis of potentiodynamic polarization study at pH – 7.2

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process[10,12-17]. 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 given in the **Table.2** and shown in **Fig-2**.When carbon steel was immersed in well water the corrosion potential was **-670** mV vs SCE. When L - Phenylalanine (250 ppm) and Zn^{2+} (5 ppm) were added to the above system the corrosion potential shifted to the noble side **-655** mV vs SCE. This indicates that a film is formed on the anodic sites of the metal surface. The formation of protective film on the metal surface is further supported by the fact that the anodic Tafel slope (b_a) increases from 115 to 170 mV. Further, the LPR value increases from 5.710 x 10^4 ohm cm^2 to 7.979 x 10^4 ohm cm^2; the corrosion current decreases from 5.805 x10^{-7} A/cm^2 to 5.003 x 10^{-7} A/cm^2. Thus, polarization study confirms the formation of a protective film on the metal surface.

4.1. Analysis of potentiodynamic polarization study at isoelectric point (pH - 5.9)

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors at isoelectric point (pH=5.9) are given in the **Table.2** and shown in **Fig.2**. When carbon steel was immersed in well water, the corrosion potential was **-657**mV vs SCE. When L - Phenylalanine (250 ppm) and Zn^{2+} (5 ppm) were added to the above system, the corrosion potential shifted to **-668** mV vs SCE. The corrosion potential is shifted cathodic side (active site). It is observed that I_{corr} value increases from 5.672 x10^{-7} A/cm^2 to 6.532 x10^{-7} A/cm^2, LPR value decreases from 5.922 x 10^4 ohm cm^2 to 5.655 x 10^4 ohm cm^2, there is no protection of metal, the metal undergoes corrosion. This is in agreement with weight loss results. This is due to the fact that at isoelectric point (pH = 5.9) there is no migration of L - Phenylalanine towards the metal surface[19,20]. Therefore amount of L - Phenylalanine transported towards the metal surface is reduced. So, metal is not protected by L - Phenylalanine. Hence there is no IE at isoelectric point.

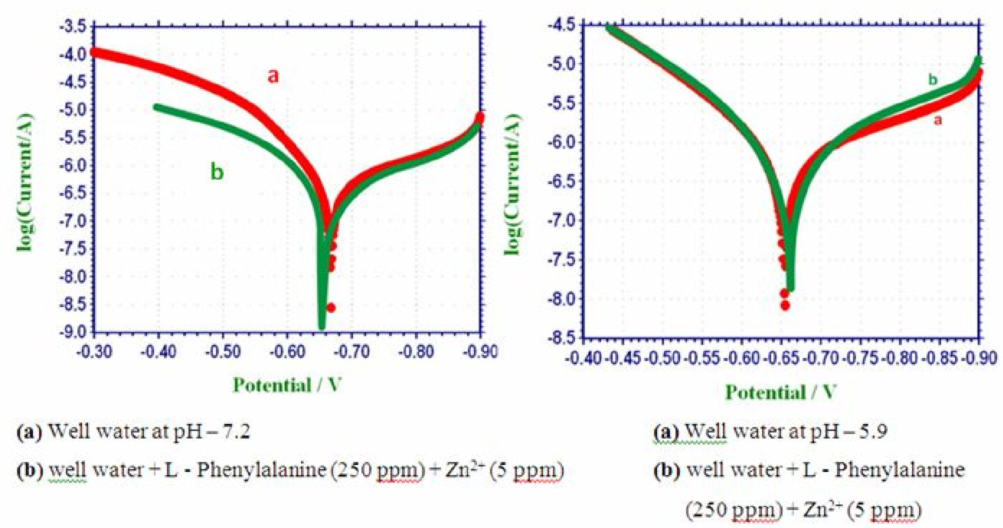


Fig-2.Polarization curves of carbon steel immersed in test solutions

Table 2: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study

System	Tafel Results				
	E_{corr} mV vs SCE	bc mV/decade	ba mV/decade	I_{corr} A/cm^2	LPR ohm cm^2
Well water	**-670**	287	115	5.805 x10^{-7}	5.710 x 10^4
Well water + L-Phenylalanine (250ppm)+ Zn^{2+} (5ppm) at pH – 7.2	**-655**	235	170	5.003 x10^{-7}	7.979 x 10^4
Well water at pH – 5.9	**-657**	204	134	5.672 x10^{-7}	5.922 x 10^4
Well water+ L-Phenylalanine (250ppm)+ Zn^{2+} (5ppm) at pH – 5.9	**-668**	277	142	6.532 x10^{-7}	5.655 x 10^4

5. Analysis of AC Impedance spectra at pH – 7.2

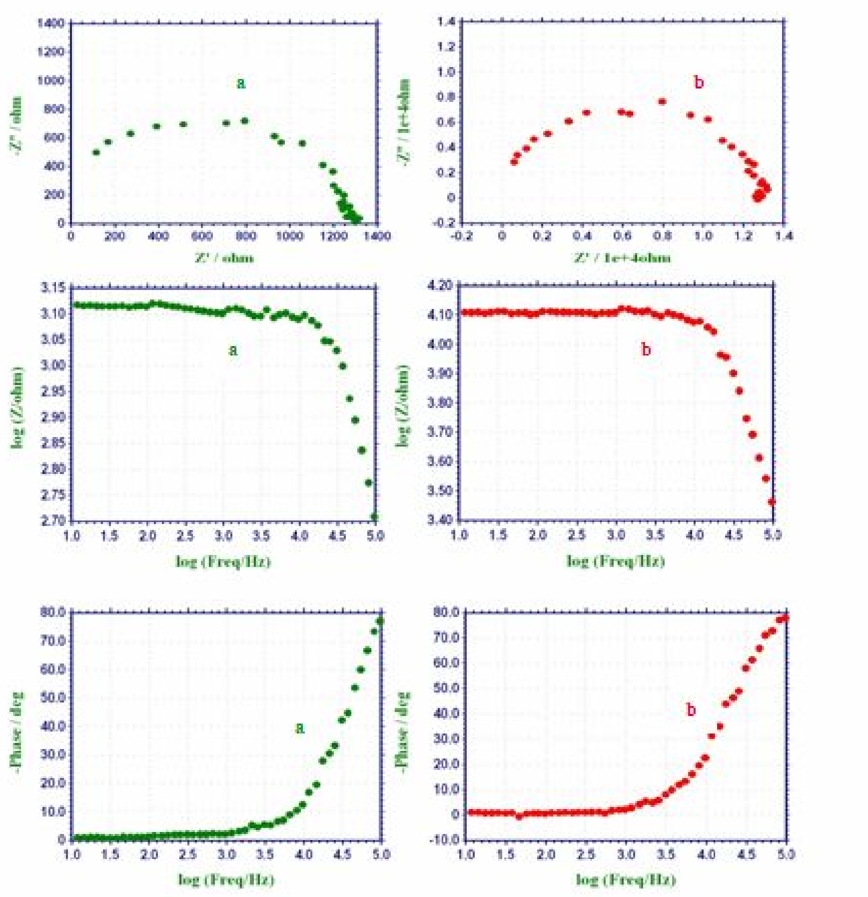


Fig-3.AC Impedance Spectra of carbon steel immersed in test solution (Nyquist plot & Impedance – Bode plot)

(a) Well water at pH – 7.2, **(b)** Well water + L - Phenylalanine (250 ppm) + Zn^{2+} (5 ppm)

5.1. Analysis of AC impedance spectra at isoelectric point (pH=5.9)

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface[21-23]. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases and the impedance log (z/ohm) value increases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L - Phenylalanine -Zn^{2+}) aregiven in the **Table – 3** and shown in **Fig-3** (Nyquist plot and Bode plot). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plot. The impedance log (z/ohm) values and Phase angle derived from Bode plot. It is observed that when the inhibitors (L - Phenylalanine (250 ppm) +Zn^{2+} (5 ppm)) are added the charge transfer resistance (R_t) increases from 1199 Ω cm^2 to 12695 Ω cm^2. The C_{dl} value decreases from 3.7348 x 10^{-9} F/cm^2 to 3.9672 x 10^{-10} F/cm^2. The impedance value [log (z/ohm)] increases from 3.142 to 4.197. These results lead to the conclusion that a protective film is formed on the metal surface. This is also supported by the fact that for the inhibitor system the phase angle increases from 77.12° to 79.68°.

The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L - Phenylalanine -Zn^{2+}) at isoelectric point are given in the **Table.3** and shown in **Fig.4** (Nyquist plot) & (Bode plot). It is observed that, when the inhibitors [L - Phenylalanine (250 ppm) + Zn^{2+} (5 ppm)] are added, the charge transfer resistance (R_t) decreases from 1600 Ω cm^2 to 1495 Ω cm^2. The C_{dl} value increases from 3.4221 x 10^{-9} F/cm^{-2} to 3.6756 x 10^{-9} F/cm^{-2}. The impedance value [log (z/ohm)] decreases from 3.288to 3.252. This is also supported by the fact that for the inhibitor system the phase angle decreases from 74.08° to 71.95°. These results suggest that a protective film is not formed on the metal surface. When a protective film is not formed, charge transfer resistance (R_t) decreases and C_{dl} increases, there is no protection of metal, the metal undergoes corrosion. This is in agreement with weight loss results. This is due to the fact that at isoelelctric point (pH=5.9) there is no migration of L - Phenylalanine towards the metal surface[19,20]. Therefore amount of L - Phenylalanine transported towards the metal surface is reduced. So, metal is not protected by L - Phenylalanine. Hence there is no IE at isoelectric point.

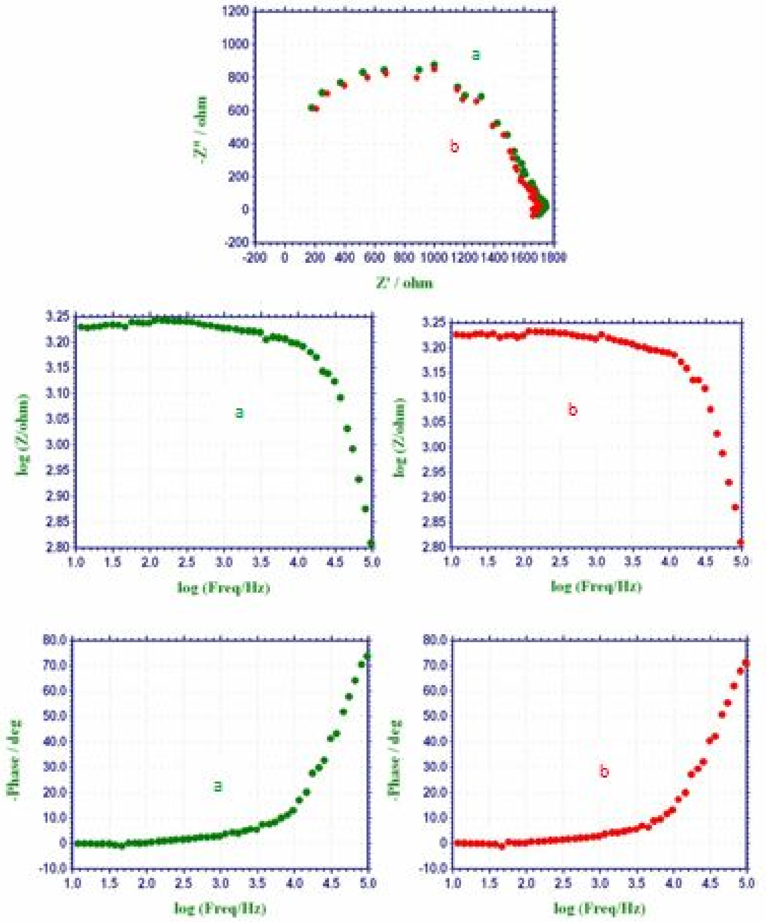


Fig-4.AC Impedance Spectra of carbon steel immersed in test solution at isoelectric point (Nyquist plot & Impedance – Bode plot)

(a) Well water at pH – 5.9 (b) Well water + L - Phenylalanine (250 ppm) + Zn^{2+} (5 ppm)

Table 3: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from AC impedance spectra.

System	Nyquist plot		Bode plot	
	R_t Ω cm^2	C_{dl} F/cm^2	Impedance value log (z/ohm)	Phase angle
Well water at pH – 7.2	1199	3.7348×10^{-9}	3.142	77.12°
Well water at pH -7.2+ L-Phenylalanine (250ppm)+Zn^{2+} (5ppm)	12695	3.9672×10^{-10}	4.197	79.68 °
Well water at pH – 5.9	1600	3.4221×10^{-9}	3.288	74.08 °
Well water at pH -5.2+ L-Phenylalanine (250ppm)+Zn^{2+} (5ppm)	1495	3.6756×10^{-9}	3.252	71.95 °

Conclusion

Weight loss study reveals that the formation consisting of 250ppm of L - Phenylalanine and 5ppm of Zn^{2+} has 95% inhibition efficiency, in controlling corrosion of carbon steel in well water and the synergistic effect exists between $Zn^{2+}$and L - Phenylalanine system. Polarization study reveals that L - Phenylalanine system function as anodic inhibitors. AC impedance spectra reveal that a protective film is formed on the metal surface. At isoelelctric point (pH=5.9) there is no migration of L - Phenylalanine towards the metal surface. Therefore amount of L - Phenylalanine transported towards the metal surface is reduced. So, metal is not protected by L - Phenylalanine. Hence there is no IE at isoelectric point.

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