INHIBITION OF CORROSION OF CARBON STEEL IN WELL WATER BY VALINE- Zn^{2+} SYSTEM

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Abstract : The environment friendly that putting off system valine -Zn^{2+} has been made observation of by weight loss careful way. A going-together effect has existence between valine and Zn^{2+} system. The rules to make made up of 300 ppm of valine and 30 ppm of Zn^{2+} offers good inhibition doing work well of 98%. Movement to opposite positions work space gives knowledge of that this rules to make functions as an anodic that putting off. AC impedance spectra gives knowledge of that a protective picture rolls is formed on the metal top. The top morphology has been got broken up (into simpler parts) by SEM. A right mechanism of corrosion inhibition is offered based on the results got from weight loss work space and electrochemical makes observations about.

IndexTerms - Carbon Steel, Valine, Synergistic effect, SEM, AC impedance, electrochemical.

I. INTRODUCTION

Corrosion is a general stretch of time used to make, be moving in different effects on one another between a material and its environment leading to degradation in the material properties. Effect on one another with ambient oxygen can cause the structuring of oxide levels via diffusion controlled growth. These may passivity the material against further oxidation

In a wet environment, aqueous corrosion can take place because of, in relation to electrochemical processes which are dependent on upon metal ion transport and reaction. Rates of change of metal and electrolytic ion concentrations, temperature, ambient pressure, and the existence of other metals, bacteria, or active units, all affect the corrosion rate.

The principles and practices of corrosion putting off in near in time years have started taking into account the being healthy and safety points to be taken into account. The use of dangerous chemicals has been limited to no touching point with the general condition. For this reason, there is a look for non-toxic eco-friendly corrosion those putting off. The use of those putting off is one of the most useful methods to keep safe (out of danger) metals from corrosion. corrosion that putting off is a chemical substance which when added to the corrosive general condition at a most good strong amount, there is a drop in the corrosion rate of metals (or) alloys importantly. Unhappily, much common corrosion those putting off are highly deadly, full of poison and health-hazardable, such as chromates [1], nitrite [2] and aromatic heterocyclic compounds [3] and so on. As an outcome of that, it is better to look for with conditions of safe those putting off. [4-6] Some persons making observations made observation of the putting off effect of general condition friendly those putting off like amino acids on metal slow destruction (by acid). [6-13] this is because of, in relation to fact that amino acids are non-toxic biodegradable relatively cheap and completely soluble in water-like thing by which something is done and produced with high cleanliness at low price.

The environmental friendly, Valine, is chosen as the corrosion inhibitor for this present work. The literature presents some studies involving amino acids having the ability to prevent the corrosion of iron,[14] steel,[15-17] aluminium,[]18-19] nickel[20] and copper.[21-25] The electrochemical studies such as polarization and AC impedance spectra[26-30] have been studied by using amino acids.

II. MATERIALS AND METHODS:

The aim of the present study is

1. To evaluate the inhibition efficiency of Valine in controlling the corrosion of carbon steel in the absence and presence of Zn^{2+}.
2. To study the mechanistic aspects by potentiodynamic polarization study, SEM.

2.1.Experimental Procedure

Carbon steel specimens (0.0267%S, 0.067%P, 0.4% Mn, 0.1%C and the rest iron) of the dimensions 1.0cm x 4.0cm x 0.2cm were polished to mirror finish and degreased with acetone and used for weight loss method an surface examination studies.

2.2.Weight loss study:

Relevant data on the well water used in this study are given in Table 1. Carbon steel specimens, were immersed in 100 ml of well water and various concentrations of Valine in the presence and absence of Zn^{2+} for a period of one day. The corrosion products were cleaned with Clarke's solution.[32]

The weight of the specimens before and after immersion was determined using Shimadzu balance AY62. The corrosion inhibition efficiency was calculated with equation

Where,

Mdd is milligram per dm^2 per day.

The corrosion inihibition efficiency of (IE%) was calculated using the formula

$$IE\ (\%) = W0\text{-}W1/W0 \times 100$$

Where,

W0 = Corrosion rate in the absence of the inhibitor

W1 = Corrosion rate in the presence of the inhibitor

2.3 Electro Chemical Studies

The electro chemical studies were doed using warm steel electrode (1 cm X 1 cm). Both the A.C impedance and potentiodynamic movement to opposite positions studies were doed using electrochemical measurement system warm steel, filled full calomel ectrode and platinum electrodes were used as the working, statement, direction and the bit for recording point's electrode separately. The three electrode organization was put in chloride solution in an electrochemical cell , both in the being away and the existence of the that putting off and let to get to a stable open circuit potential (OCP).The impedance measurements were then doed over frequency range of 100 kHz to 0.01Hz and the Nyquist makes line pictures were got. The values of the go forward give property in law stopping effect (Rct) and times level capacitance (Cd1) were worked out from these secret designs.

The charge transfer resistance is the resistance offered by the inhibitor film and a higher value of R_{ct} indicates insulation of the metal from the aggressive ions present in the solution. So, a higher R_{ct} value indicates a less conducting surface, which in turn, implies less corrosion. From the modified Stern–Geary

$$I_{corr} = (b_a\, b_c) / 2.303\ (b_a+b_c)\ R_{ct}$$

Where,

ba = Anodic Tafel slope,

bc = Cathodic Tafel slope,

Icorr = Corrosion current

Rct = Charge transfer resistance

Hence a large value of R_{ct} implies a lower i_{corr} and is indicative of lower corrosion rate. Since the maximum on the Nyquist semi-circle [3] satisfies the equation,

Where F_{max} is the maximum frequency on the Nyquist semicircle.

2.4.Surface analysis by Scanning Electron Microscopy (SEM):

For morphological study, surface features of mild steel were examined after exposure to well water after one day with and without inhibitor. JEOL JSM – 5500 Scanning electron microscope was used for this investigation.

3. RESULT DISCUSSIONS:

3.1. Analysis of weight loss study:

The values of corrosion rate and rate on a hundred putting off doing work well were worked out from weight loss careful way at different strong amount of valine water-like answer that is well water after 1 day immersion stretch of time at room temperature. It was made observations that valine the slow destruction (by acid) of carbon steel in well water at different strong amount used in work space. The greatest point putting off doing work well 68% was made clear at 300 ppm strong amount of valine the being away of Zn^{2+} and further increasing that putting off strong amount does not change IE%. in fact, slow destruction (by acid) rate values of carbon steel drops from 0.1787 (mmpy) to 0.1203 (mmpy) on the addition of 50 ppm to 300 ppm of valine the being away of Zn^{2+} ions. When the strong amount of Zn^{2+}ions increases from 10ppm-20ppm to 30 ppm the putting off doing work well slightly increases. The greatest point putting off doing work well 98% was made clear at 300 ppm strong amount of valine and 30 ppm of Zn^{2+}ions and slow destruction (by acid) rate values of carbon steel drops from 0.0948 (mmpy) to 0.0072 (mmpy) The increased putting off doing work well (IE%) and dropped slow destruction (by acid) rate might be because of, in relation to the outcome of increased joining of a substance on to a body and increased amount covered of valine the warm steel top with increasing strong amount valine It is clear that valine showed good putting off for carbon steel slow destruction (by acid) in well water answers because has nitrogen and oxygen having in it putting off for carbon steel slow destruction (by acid) in well water answers because has nitrogen and oxygen having in it able to use groups.

Table:1.Corrosion Rate (CR) and Inhibition Efficiency (IE) of carbons steel immersed in well water containing in the presence and absence of inhibitor:

Valine (ppm)	Zn^{2+}	Zn^{2+}	Zn^{2+}	Zn^{2+}

	(0 ppm)		(10 ppm)		(20 ppm)		(30 ppm)	
	IE %	CR (mmpy)	IE %	CR (mmpy)	IE %	CR (mmpy)	IE %	CR (mmpy)
0	-	0.4324	10	0.3346	16	0.3045	21	0.2876
50	51	0.1787	62	0.1387	68	0.1166	74	0.0948
100	54	0.1628	65	0.1278	72	0.1021	77	0.0839
150	57	0.1569	70	0.1093	75	0.0912	83	0.06212
200	60	0.1460	73	0.0984	79	0.0766	89	0.0400
250	63	0.1351	76	0.0875	82	0.0745	94	0.0218
300	67	0.1203	80	0.0727	85	0.0436	98	0.0072

3.2.SYNERGISM PARAMETER:

Synergism parameter is calculated to evaluate the synergistic effect existing between inhibitors. The synergism parameter (SI) can be calculated using the relationship given by *aramaki* and hackerman.

$$S_I = 1\text{-}I_{1+2}/1\text{-}I'_{1+2}$$

Where, $I_{1+2} = (I_1+I_2)-(I_1\times I_2)$

I_1 = Surface coverage of inhibitor (Valine)

I_2 = surface coverage of inhibitor (Zn^{2+})

I'_{1+2} = combined surface coverage of inhibitors (Valine) and (Zn^{2+})

IE/100 = surface coverage

When $S_I>1$,synergistic effect exist between the two inhibitors. In case of $S_I<1$,negative interaction takes place between the two inhibitors, (i.e, CR increases). The calculated synergism parameter values for Valine and Zn^{2+}. Synergism parameter (S_I) for the formulation consisting of 300 ppm of Valine and 30 ppm of Zn^{2+} ions are 13.035, which is greater than one. This shows that the synergistic effect exists between Valine and Zn^{2+}.

Table 2.Synergism parameter for Valine (300 ppm) - Zn^{2+} (30 ppm) system in carbon steel immersed in well water for one day:

Valine (ppm)	Zn^{2+} (30 ppm)	I_1	I_2	(I'_{1+2})	S_I	IE%
50	30	0.51	0.21	0.74	1.4880	74
100	30	0.54	0.21	0.77	1.5800	77
150	30	0.57	0.21	0.83	1.9982	83
200	30	0.60	0.21	0.89	2.8727	89
250	30	0.63	0.21	0.94	4.8716	94
300	30	0.67	0.21	0.98	13.035	98

3.3. Analysis of polarization curves:

Polarization study has been used to detect the formation of protective film on the metal surface during corrosion inhibition process [57-60]. The calculated corrosion parameters such as corrosion potential (Ecorr) , Tafel slopes Anodic slope (ba) and cathodic slope (bc), Linear polarization resistances (LPR) and Corrosion current (Icorr) values are given in the Table 3. The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors.

When carbon steel is immersed in well water, the corrosion potential is-784 mV vs SCE. The formulation consisting of 300 ppm Valine and 30 ppm Zn^{2+} shifts the corrosion potential is -750 mV vs SCE. This suggests that the Valine–Zn^{2+} formulation functions as an anodic inhibitor, controlling the anodic reaction predominately. The corrosion current value and LPR value for well water 4.098×10^{-6} A/cm^2 and 3130×10^{-3} Ω cm^2. For the formulation of Valine (300 ppm) + Zn^{2+} (30 ppm),the corrosion current value has decreased to 5.3750×10^{-6}A/cm^2 and the LPR value has increased to 7951×10^{-3} Ω cm^2. This indicates that a protective film is formed on the metal surface. When a protective film is formed on the metal surface LPR value increases and corrosion current value decreases [38].

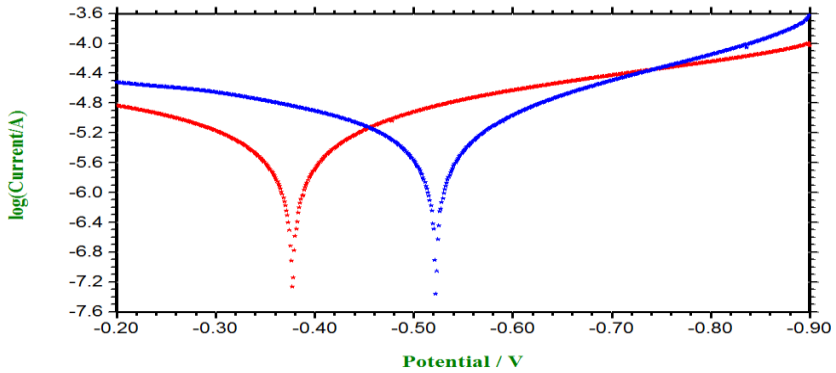

Fig 1.Polarization curves of carbon steel immersed in well water
a)Well water b) 300 ppm of Valine + 30 ppm of Zn^{2+} + well water

Table 3. Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitor obtained by polarization method:

Valine(ppm)	Zn^{2+} (ppm)	Ecorr (mV vs SCE)	Icorr (A/cm2)	ba (mV dec-1)	Bc (mV dec-1)	LPR (Ωcm^2)
0	0	-377	4.098×10^{-6}	191.53	216.11	3130×10^{-3}
300	30	-522	5.3750×10^{-6}	236.20	168.31	7951×10^{-3}

3.4.Analysis of AC impedance spectra of Valine-Zn^{2+}:

AC impedance spectra have been used to detect the formation film on the metal surface [61, 64- 66]. The AC impedance spectra of carbon steel immersed in well water in the absence and presences of inhibitors. The impedance parameters such as Charge transfer resistance (Rct) and Double layer capacitance (Cdl) values are given in the Table 4. If a protective film formed the charge transfer resistance (Rct) and double layer capacitance value decreases. It is clear from the plots that the impedance response of carbon steel significantly changed after addition of the inhibitors. The impedance diagrams obtained almost semicircular appearance. This indicates that the corrosion of carbon steel in aqueous solution is mainly controlled by a charge transfer process [53]. The deviation from the perfect semicircle shape is due to the frequency dispersion of interfacial impedance. This anomalous behavior is generally due to the non - homogeneity of the metal surface arising from surface roughness or interfacial phenomena.

From the above table the Rct value is 57.56 Ω cm^2 and Cdl value is 5.1500× 10^{-8} µF/cm2. When Valine and Zn^{2+} are added to well water, Rct value increases from 57.56 Ω cm^2 to 237.50Ω cm^2. The Cdl value decreases from 5.1500× 10^{-8}µF/cm2 to 4.3499× 10^{-8}. This confirms that the formation of protective film on the metal surface. This accounts for the very high Inhibition Efficiency of Valine – Zn^{2+} system.

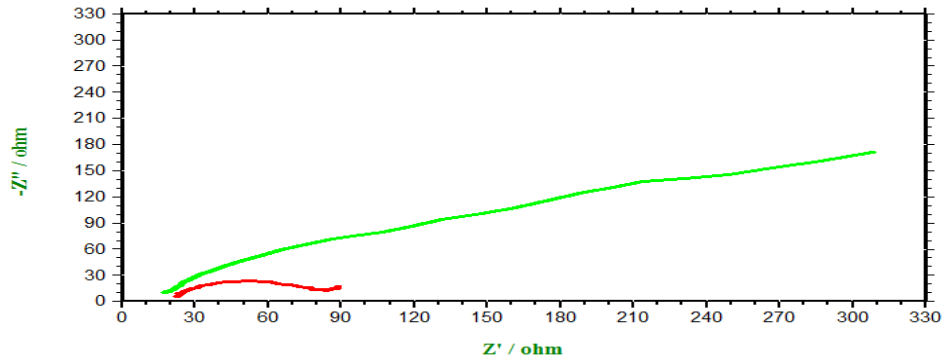

Fig.2. AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots)
(a) Well water (b) Well water + Valine (300 ppm) + Zn^{2+} (30 ppm)

Table 4.Impedance parameters of carbon steel immersed in well water in the absence and presences of inhibitors obtained by AC impedance spectra

Valine (ppm)	Zn^{2+} (ppm)	Rct (Ωcm^2)	CdI ($\mu F/cm^2$)	IE%
0	0	57.56	5.1500×10^{-8}	-
300	30	237.50	4.3499×10^{-8}	98

3.5. SCANNING ELETRON MICROSCOPE:

SEM analysis was carried out to know additional information about the film Surface morphology of formation.

Figure a for polished carbon steel and Figure b and c show SEM photographs of mild steel specimen in the absence and presence of the inhibitor system 300 ppm of Valine, 30 ppm of Zn^{2+}. It can be seen from Figure b shows that the surface is severely corroded and there is formation of different forms of corrosion products (iron oxides) on the surface in the absence of inhibitor. It further shows that the corrosion products appear very uneven and the surface layer is too rough. Figure c shows that the surface of mild steel immersed in the inhibitor solutions are having smooth surfaces. It is important to stress that when the inhibitor is present in the solution, the morphology of the mild steel surface are quite different from the previous one.

The protective layer is randomly observed on the mild surface and the interpretation is that due to adsorption of inhibitor on the mild steel surface integrating into the passive film in an ordered manner has blocked the active site available in the metal surface of the mild steel. SEM analysis shows the protective nature of the surface film.

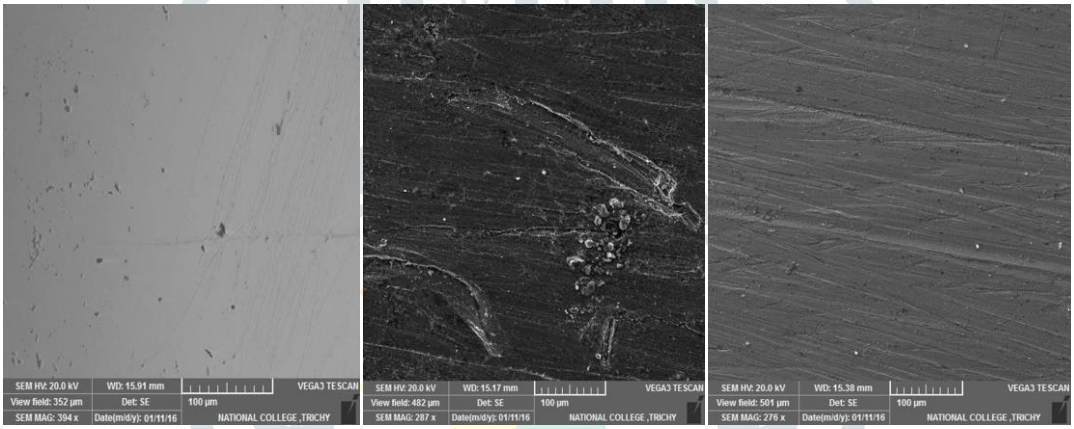

Fig.3.SEM images (100 µm) of a) Polished carbon steel (control) b) Carbon steel immersed in well water (blank) c) Carbon steel immersed in well water containing 300 pmm of Valine and 30 ppm of Zn^{2+}.Zn^{2+} systems:

The inhibitor formulation consisting 300 ppm Valine, 30 ppm Zn^{2+} ion afforded an inhibition efficiency of 98% was achieved. Further, this inhibitor combination acts as a mixed inhibitor, predominantly cathodic in nature. The corrosion inhibition is established due to the formation of an inhibiting film, which has a very high charge transfer resistance. SEM, provide a pictorial representation on the nature of surface film formed in the absence and presence of inhibitor system. The protective film consists of [Fe^{2+}- Valine -Zn^{2+}] complex, small amounts of iron oxide, hydroxide and zinc hydroxide.

4.CONCLUSION

The inhibition efficiency (IE) of Valine Zn^{2+} system in controlling corrosion of carbon steel in well 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 300ppm of Valline and 30ppm of Zn^{2+} has 98% inhibition efficiency in controlling corrosion of carbon steel immersed in well water.
- Synergistic parameters suggests that a synergistic effect exists between Valine and Zn^{2+}.
- Polarization study reveals that this system functions as mixed type of inhibitor controlling the cathodic reaction and anodic reaction to equal extents
- AC Impedence spectra reveals that a protective film is formed on the metal surface.
- The SEM study proves that the protective film formed on the metal surface.

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