THE CORROSION INHIBITION OF ISONICOTINAMIDE (ISN) - Zn^{2+} SYSTEM CONTROLS THE CORROSION OF CARBON STEEL IN 1 M HYDROCHLORIC ACID SOLUTION

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The corrosion inhibition efficiency of Isonicotinamide (ISN) in controlling the corrosion of carbon steel in 1 M hydrochloric acid solution (HCl) in absence and presence of Zn^{2+} has been studied by weight loss method. Weight Loss study reveals that the formulation consisting of 10 ppm of ISN and 10 ppm of Zn^{2+} has 78% inhibition efficiency. The results of polarisation study shows that the formulation function controls the anodic reaction predominantly. The AC impedance spectra reveal that a protective film formed on the metal surface. FTIR spectrum reveal that the protective film consists of Fe^{2+}-ISN complex on the anodic sites of metal surface and $Zn(OH)_2$ formed on cathodic sites of metal surface.

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INTRODUCTION

Corrosion is a natural phenomenon involving the reversion from metallic to compound state. So it becomes evident that corrosion cannot be fully prevented instead it can be controlled to a greater extent. Many researchers have used various nitrogen-containing compounds in their corrosion inhibition investigations. These compounds included quaternary ammonium salts,[1-7] polyamino-benzoquinone polymers,[8] azoles,[9-16] substituted aniline-N-salicylidenes,[17] amides,[18,19] heterocyclic compounds[20], and cationic surfactants.[21,22]

The present work is undertaken:

-To evaluate the influence of isonicotinamide (ISN) with Zn^{2+} on corrosion behavior of carbon steel immersed in 1 M HCl solution by weight-loss method.

-To evaluate the type of inhibitor by polarization study.

-To evaluate the protective film by AC impedance spectroscopic study.

-To analyze the nature of protective film formed on the carbon steel by FTIR spectra.

METHODS AND MATERIALS

Preparation of specimens

Carbon steel specimens (0.0267% sulphur, 0.06% phosphorous, 0.4% manganese, 0.1% carbon and the rest iron) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Weight-loss method

Carbon steel specimens in triplicate were immersed in 100 ml of 1 M HCl solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one hour. The weight of the specimens before and after immersion was determined using Shimadzu balance, AY62 model. The corrosion products were cleansed with Clarke's solution.[23] From the change in weight of the specimens, corrosion rates were calculated with the help of the following relationship:

$$CR = \frac{\Delta m}{A * t} \quad (1)$$

where

CR - corrosion rate

Δm - loss in weight (mg)

A - surface area of the specimen (dm^2)

t - period of immersion (days)]

The inhibition efficiency (IE, %) was then calculated using the equation

$$IE = 100\left(1 - \frac{W_2}{W_1}\right) \quad (2)$$

where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

Potentiodynamic polarization study

Polarization studies were carried out in an H & CH electrochemical work station impedance analyzer model CHI660A. A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance study

The instrument used for polarization was also used for AC impedance study. The cell set up was the same as that used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance(R_t) and the double layer capacitance(C_{dl}) were calculated.

Surface Examination

The carbon steel specimens were immersed in various test solutions for a period of one day, after one day the carbon steel specimen were taken out and dried.

The nature of the film formed on the surface of metal specimen was analysed by FTIR spectroscopic study.

FTIR Spectra

FTIR spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

RESULTS AND DISCUSSION

Analysis of results of weight loss method

The corrosion inhibition efficiency of carbon steel in the absence and presence of various concentrations of inhibitor obtained by the weight - loss method in one hour system are given in the Table 1 to 3.

The corrosion rates (*CR*) are also given in these tables.

The weight - loss method reveals that the isonicotinamide alone shows some inhibition efficiency at higher concentration. But Zn^{2+} alone is corrosive nature. For example 10 ppm of ISN alone is 12 inhibition effciency; 10 ppm of Zn^{2+} alone is corrosive nature. But it is interestingly noted that the formulation consisting of 10 ppm of ISN and 10 ppm of Zn^{2+} system shows 78% inhibition effciency.

This is due to the fact that there is synergistic effect exist between ISN and Zn^{2+} system. This means that the mixed inhibitors shows good inhibition efficiency than individuals.

Table 1. Corrosion rates (*CR*) of Carbon steel in 1 M HCl in the presence and absence of inhibitor and obtained by weight loss method

No	ISN, ppm	Zn^{2+}ppm	*IE*, %	*CR*, mdd
1	0	0	-	36.00
2	10	0	12	31.68
3	20	0	15	30.60
4	30	0	18	29.52
5	40	0	22	28.08
6	50	0	26	26.64
7	60	0	28	25.92

Table 2. Corrosion rates (*CR*) of Carbon steel in 1 M HCl in the presence and absence of inhibitor and obtained by weight loss method

S.No	ISN, ppm	Zn^{2+}, ppm	*IE*, %	*CR*, mdd
1	0	0	-	36.00
2	0	10	-8	38.88
3	0	20	-12	40.32
4	0	30	-14	41.04
5	0	40	-17	42.12
6	0	50	-17	42.12
7	0	60	-20	43.20

Analysis of potentiodynamic polarization study

The polarization curves of carbon steel immersed in ISN-HCl solution in the presence and absence of inhibitors are shown in Figure 1. The corrosion parameters are given in Table 4. When carbon steel immersed in isonicotinamide-1 M HCl solution, corrosion potential (E_{corr}) -664 mV vs SCE. The formulation consisting of 10 ppm of isonicotinamide and 10 ppm of Zn^{2+} shifts the corrosion potential to -565 mV vs SCE, ie corrosion potential shifts to anodic direction (from -664 mV to -565 mV). This suggest that the anodic reaction is controlled predominantly indicating the reduction resolution of metal as more isonicotinamide molecules are transported to the anodic sides in the presence Zn^{2+} ions.

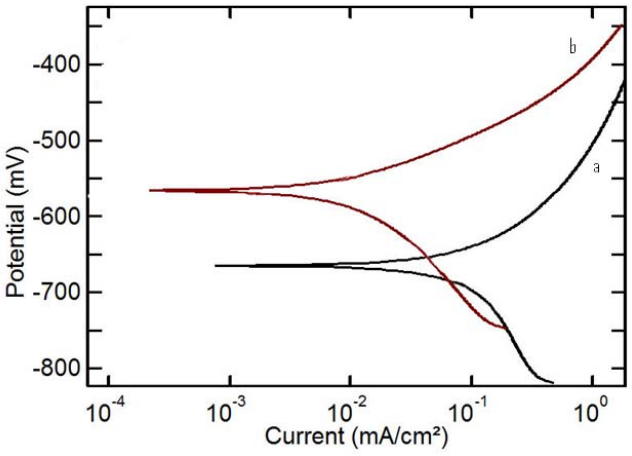


Figure 1. Polarization curves of carbon steel immersed in various test solution: a) 10 ppm of ISN + 1 M HCl; b) 10 ppm of ISN + Zn^{2+} 10 ppm +1 M HCl

Table 3. Corrosion rates (*CR*) of Carbon steel in 1 M HCl in the presence and absence of inhibitor and obtained by weight loss method

S.No	ISN, ppm	Zn^{2+}, ppm	*IE*, %	*CR*, mdd
1	0	0	-	36.00
2	10	10	78	7.92
3	10	20	64	12.96
4	10	30	35	23.40
5	10	40	24	27.36
6	10	50	20	28.80
7	10	60	12	31.68

Now the shifts in the anodic cathodic slopes can be compared. The addition of 10 ppm of Zn^{2+} shifts the anodic slope value 64 mV decade^{-1} to 56 mV decade^{-1}, will the corresponding shift cathodic slope is from 91 mV decade^{-1} to 106 mV decade^{-1}. Thus formulation of 10 ppm of isonicotinamide and 10 ppm of Zn^{2+} controls the anodic predominately and to some extent controls the cathodic reaction by the formation $Zn(OH)_2$ and cathodic sides of the metal surface.

The corrosion current (I_{corr}) for isonicotinamide is 0.04343 A cm^{-2}. It is defused to 0.007224 A cm^{-2} by the addition 10 ppm of Zn^{2+}. The current of the iron dissolution is decreased significantly indicating that the metal surface was passive by the formed inhibitor layer. The passivity ion is probably due to the formation of isonicotinamide – Fe^{2+} surface layer. The significant reduction in corrosion current for inhibitor formulation may indicate more adsorption of the inhibitors and better inhibitions performance. This result suggests that a protective film (isonicotinamide – Fe^{2+}-complex) is formed on the metal surface. This protects the metal from corrosion.

Table 4 : Corrosion parameters of carbon steel immersed in various test solution obtained by polarization method.

System	Ecorr, mV vs SCE	b_c,	b_a,	Icorr, A cm^{-2}
		mV decade^{-1}		
10 ppm of ISN + 1 M HCl	-664	64	91	0.04343
10 ppm of ISN + 10 ppm of Zn^{2+} + 1 M HCl	-565	56	106	0.007224

Analysis of AC impedance spectra

The AC Impedance spectra of carbon steel immersed in various test solution are shown in Figure 2. The AC impedance parameters, namely the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) are given in Table 5.

Impedance parameters for corrosion of carbon steel immersed in 1 M HCl in the presence and absence of inhibitor system obtained from AC impedance curves.

Table 5. Corrosion parameters of carbon steel immersed in various test solution obtained by AC impedance spectra.

S.No.	System	R_t, Ω cm^2	C_{dl}, F cm^{-2}
1.	ISN 10 ppm + 1 M HCl	0.675	6.980 x 10^{-4}
2.	ISN 10 ppm+ Zn^{2+} 10 ppm + 1 M HCl	1.24	2.375 x 10^{-4}

AC Impedance parameters namely a charged transfer resistance (R_t) and the double layer capacitance(C_{dl}) are given in Table 5. When carbon steel immersed in 10 ppm of isonicotinamide and 1 M HCl, the R_t value is found to be 0.675 Ω cm^2 and C_{dl} value is 6.980 x 10^{-4} F cm^{-2}. When 10 ppm of Zn^{2+} is added to the above system, the R_t value increases from 0.675 Ω cm^2 to 1.24 Ω cm^2 and C_{dl} value decreases from 6.980 x 10^{-4} F cm^{-2} to 2.375 x 10^{-4} F cm^{-2}. The increased R_t values and decreased double layer capacitance value obtained from impedance studies justify the good performance of ISN as an inhibitor in 1 M HCl. This behavior source that the protective film obtained act as a barrier to the corrosion process that clearly existence and formation of the protective film on the metallic surface.[24,25]

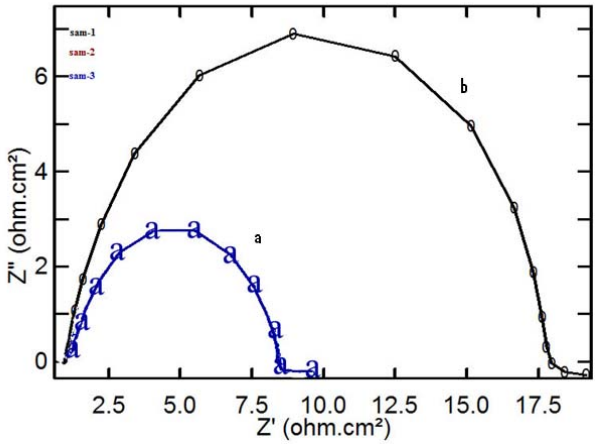
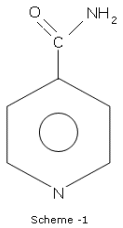


Figure 2. AC impedance spectra of carbon steel immersed in various test solution, a) 10 ppm of ISN + 1 M HCl, b) 10 ppm of ISN + Zn^{2+} 10 ppm + 1 M HCl

Surface analysis

The structure of isonicotinamide is shown in Scheme 1.



Scheme -1

It contains C=O group, C-N group and N-H Stretching vibrations group.The protective film formed on the surface of the metal in the presence of isonicotinamide system and isonicotinamide – Zn^{2+} system in 1 M HCl has been analysed by FTIR spectroscopy.

Analysis of FTIR spectra

The FTIR spectrum (KBr) of pure isonicotinamide is shown in figure 3a. C=O stretching frequency appears at 1682 cm^{-1}. The C-N stretching frequency appears at 1121 cm^{-1} The N-H stretching frequency appears at 3362 cm^{-1}. The FTIR spectrum (KBr) of the film formed on the surface of the metal after immersion, the solution containing 10 ppm of isonicotinamide and 10 ppm Zn^{2+} in 1 M HCl is shown in figure 3b. It is found that C=O stretching frequency of isonicotinamide decreased from 1682 cm^{-1} to 1617 cm^{-1}. The C-N stretching frequency of isonicotinamide has decreased from 1121 cm^{-1} to 1018 cm^{-1}. The N-H stretching frequency of isonicotinamide has decreased from 3362 cm^{-1} to 3359 cm^{-1}.

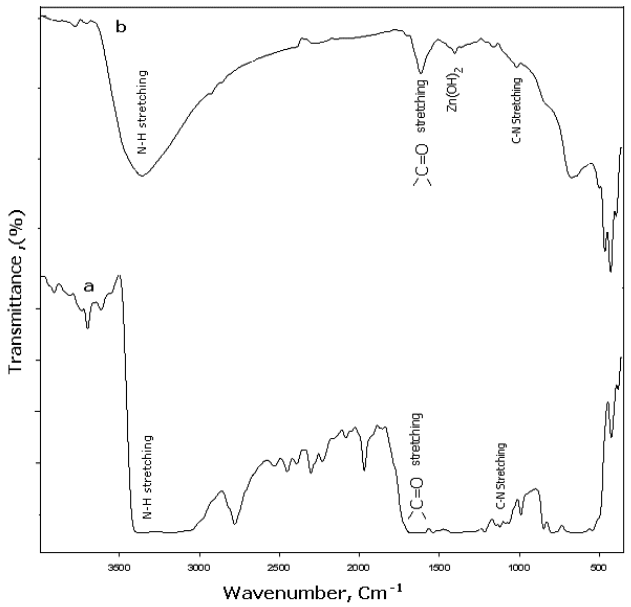


Figure 3. FTIR spectra; a) Pure solid Isonicotinamide; b) Film formed on the metal surface after the immersion of the solution of 10 ppm of Isonicotinamide and 10 ppm Zn^{2+} in 1 M HCl

It is interfered that isonicotinamide has coordinated with Fe^{2+} oxygen atom and nitrogen atom resulting in the formation of Fe^{2+}- ISN complex on the anode sites of the metal surface.[26,27] The bond at 1401 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface.

CORROSION INHIBITION MECHANISM FOR (ISN- Zn^{2+}) SYSTEM

The weight – loss study reveals that the formulation consisting of 10 ppm of Zn^{2+} and 10 ppm of isonicotinamide has 78% inhibition efficiency. The FTIR spectrum reveals that the protective film consist of Fe^{2+} - isonicotinamide complex and $Zn(OH)_2$. In order to explain the above observations, the following mechanism of corrosion inhibition is proposed.[28-34]

When the environment consisting of 10 ppm of Zn^{2+} and 10 ppm of isonicotinamide are prepared, there is a formation of Zn^{2+} - ISN complex.

When carbon steel is introduced in this solution there is diffusion of Zinc complex towards the metal surface.

On the metal surface zinc complex is converted into iron complex on the anodic site.

$$Zn^{2}\text{- ISN+ } Fe^{2+} \rightarrow Fe^{2+}\text{-ISN+ } Zn^{2+}$$

The released Zn^{2+} combined with OH^- to form $Zn(OH)_2$ on the cathodic sites.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$$

Thus, the protective film consists of Fe^{2+}-ISN and $Zn(OH)_2$.

CONCLUSION

The weight – loss study reveals that the formulation consisting of 10 ppm of Zn^{2+} and 10 ppm of isonicotinamide has 78% inhibition efficiency. Synergistic effect exists between isonicotinamide and Zn^{2+} system.

The results of polarization study suggest that the formulation of 10 ppm of ISN and 10 ppm of Zn^{2+} system controls the anodic reaction predominantly.

The AC impedance spectral studies reveal that the protective film obtained act as a barrier to the corrosion process that clearly existence and formation of the protective film on the metallic surface.

The protective film consists of Fe^{2+} - ISN and $Zn(OH)_2$ by FTIR spectroscopy.

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