

Inhibiting Effect of Nicotinic Acid Hydrazide on Corrosion of Aluminum and Mild Steel in Acidic Medium

J. Ishwara Bhat* and Vijaya D. P. Alva†

Department of Chemistry, Mangalore University, Mangalagangothri, Karnataka, India. *E-mail: bhatij@yahoo.com

†Department of Chemistry, Shree Devi Institute of Technology, Karnataka, India

(Received December 12, 2013; Accepted January 8, 2014)

ABSTRACT. The corrosion behavior of aluminum and mild steel in hydrochloric acid medium was studied using a nicotinic acid hydrazide as inhibitor by potentiodynamic polarization, electrochemical impedance spectroscopy technique and gravimetric methods. The effects of inhibitor concentration and temperature were investigated. The experimental results suggested, nicotinic acid hydrazide is a good corrosion inhibitor for both aluminum and mild steel in hydrochloric acid medium and the inhibition efficiency increased with increase in the inhibitor concentration. The polarization studies revealed that nicotinic acid hydrazide exhibits mixed type of inhibition. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the aluminum and mild steel surface and inhibits corrosion by blocking the reaction sites on the surface of aluminum.

Key words: Nicotinic acid hydrazide, Aluminum, Mild steel, Corrosion

INTRODUCTION

The subject of material corrosion has gained considerable importance during the last few decades because of the increasing awareness of the enormous losses caused by corrosion damage. Many of the corrosion problems existing in the industries are due to the aggressive acid environment present which lead to the corrosion of respective metals of constructions. Development of methods to control such corrosion is a challenge to chemists and scientists, working in this area.¹

Corrosion of aluminum and mild steel in acidic aqueous solutions is one of the major areas of concern in many industries where acids are widely used for applications such as acid pickling, acid cleaning, acid descaling and oil well acidizing. Due to the general aggressiveness of acid solution the materials of construction are getting corroded easily. A large number of methods have been employed to understand the practical problem of corrosion and its control.²⁻¹²

Among several methods devised to control metallic corrosion, the uses of inhibitors often remain the most practical and cost effective means.¹³ It is possible to reduce the corrosion rate to a safe level by adding inhibitors which influence the kinetics of the electrochemical reactions and thereby modify the metal dissolution in acids. The corrosion inhibitors bring down the rate of corrosion to a greater extent, even when added in small quantities to the corrosive environment. The use of organic compounds to inhibit corrosion of metals in acidic environments is well estab-

lished.¹⁴⁻¹⁸ Most of the effective and efficient organic inhibitors are those compounds that have π bonds and contain hetero atoms such as O, N, S and P which allow adsorption on the metal surface.^{19,20} The organic inhibitors function through adsorption on the metal surface blocking the active sites of metal dissolution and/or hydrogen evolution, thus retarding overall rate of corrosion in aggressive environment.²¹

Although existing data show that, many organic inhibitors have good anticorrosive ability, some of them are highly toxic to both human beings and environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been of global concern. Due to this interest is still growing to exploit environmentally acceptable corrosion inhibitors. Hence the investigation of non-hazardous corrosion inhibitors is of great importance.

Nicotinic acid hydrazide is an important intermediate for the synthesis of organic and pharmaceuticals compounds and also useful as an antitubercular, antimicrobial and antimycobacterial agent. The aim of the present investigation is to study the effect of nicotinic acid hydrazide as a potential corrosion inhibitor for aluminum and mild steel in HCl medium.

EXPERIMENTAL

The A-63400 aluminum samples and IS-2062 mild steel samples were used for the corrosion study, whose chemical composition is as given in *Table 1* and *Table 2*. Samples

Table 1. Chemical composition of A-63400

Element	Cu	Mg	Si	Fe	Mn	Zn	Cr	Tl	Al
wt%	0.1	0.4–0.9	0.3–0.7	0.6	0.3	0.2	0.2	0.1	Remainder (96.9–97.8%)

Table 2. Chemical composition of IS-2062

Element	C	Mn	S	P	Si	Fe
wt%	0.18	0.6	0.05	0.04	0.1	Remainder (99.03%)

were cut into an overall apparent size with dimensions $1 \times 0.5 \times 0.06$ inch for aluminum and $1 \times 0.3 \times 0.06$ inch for mild steel. Test materials were polished with different emery papers up to 1000 grade, cleaned with acetone, washed with double distilled water and properly dried prior to exposure. Analar grade HCl and double distilled water were used to prepare all solutions. Nicotinic acid hydrazide (F.W. 137.14) from Sigma Aldrich Corporation was used for the study.

Weight loss measurements were performed on aluminum and mild steel coupons in 1 M hydrochloric acid solution with different concentrations of the inhibitor. Weight loss of the aluminum and mild steel coupons was noted after an immersing period of 4 hours and 24 hours respectively.

Electrochemical tests were carried out with a CH-analyser model-CH1660D. The cell arrangement used was a conventional three electrode cell with platinum counter electrode, saturated calomel electrode as reference electrode and test material (Al/mild steel) as working electrode. The test material was covered by epoxy adhesive-araldite, so that only 1 cm^2 area was in contact with the solution. Polarisation curves were recorded potentiodynamically at the scan rate of 1 mV/s, in the range of +250 mV

to –250 mV versus Open Circuit Potential (OCP). Impedance was measured over a frequency range of 1 MHz to 0.05 Hz using an amplitude of 10 mV peak to peak using AC signal. The surface of the aluminum and mild steel were analysed after the corrosion tests by an optical microscope and scanning electron microscope respectively.

RESULTS AND DISCUSSION

Polarisation Measurements

The electrochemical parameters like corrosion current density (i_{corr}), corrosion potential (E_{corr}), corrosion rate (C.R) and inhibition efficiency (I.E%) values calculated from potentiodynamic polarization measurements of aluminum and mild steel in 1M HCl containing various concentrations of the nicotinic acid hydrazide at 303 K are given in Table 3 and Table 4 respectively.

The inhibition efficiency (I.E%) is calculated by the following equation:²²

$$\text{I.E (\%)} = \left(1 - \frac{i'_{corr}}{i_{corr}}\right) \times 100 \quad (1)$$

where, where i'_{corr} and i_{corr} are the corrosion currents in the presence and absence of the inhibitor respectively.

Table 3. Experimental electrochemical parameters for corrosion of aluminum in 1 M HCl solution in the presence of at 303 K by polarization method

Inhibitor (ppm)	$i_{corr} \times 10^{-3}$ (A)	$C_R \times 10^3$ (mil/year)	E_{corr} (mV)	β_a (V/dec)	β_c (V/dec)	I.E (%)
0	41.97	17.99	–760	0.196	0.215	–
10	7.179	3.077	–762	0.183	0.176	82.89
50	3.18	1.363	–757	0.165	0.165	92.42
100	2.79	1.196	–762	0.162	0.180	93.35
250	1.406	0.6026	–768	0.140	0.161	96.64

Table 4. Experimental electrochemical parameters for corrosion of mild steel in 1 M HCl solution in the presence of inhibitor at 303 K by polarization method

Inhibitor (ppm)	i_{corr} (mA)	$C_R \times 10^2$ (mil/year)	E_{corr} (mV)	β_a (V/dec)	β_c (V/dec)	I.E (%)
0	2.81	13.2	–511	0.196	0.136	–
50	0.92	4.19	–501	0.143	0.130	67.29
100	0.73	3.31	–505	0.141	0.116	74.19
250	0.55	2.49	–501	0.127	0.115	80.56
500	0.24	1.08	–504	0.128	0.134	91.59

Corrosion Rate (C.R) in MPY (mils penetration per year) is calculated using:²³

$$\text{C.R} = K \frac{ai}{nD} \quad (2)$$

where, a is the atomic weight of the metal, i is the current density in A/cm^2 , n is the number of electrons lost, D is the density in g/cm^3 and K is a corrosion constant depending on the unit of corrosion rate (for MPY, $K = 1.288 \times 10^5$).

Fig. 1 and Fig. 2 show the potentiodynamic polarization curves for aluminum and mild steel respectively, in 1 M HCl containing various concentrations of the inhibitor at 303 K. The addition of the inhibitor to the acid solution shifts anodic polarization curves to more positive

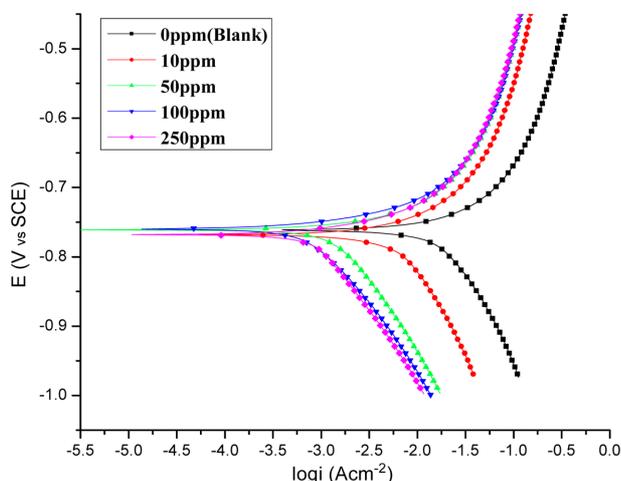


Figure 1. Plot of E vs $\log i$ for corrosion of aluminium in 1 M HCl solution at 303 K containing various concentrations of inhibitor.

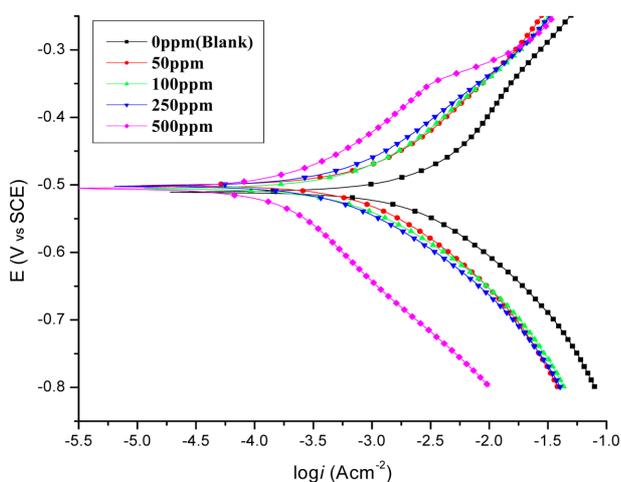


Figure 2. Plot of E vs $\log i$ for corrosion of mild steel in 1 M HCl solution at 303 K containing various concentrations of inhibitor.

values and cathodic polarization curves to more negative values. The increase in the concentration of the inhibitor increased the polarization shift. The corrosion current (i_{corr}) was found to decrease with increase in inhibitor concentration indicating, the increased inhibition efficiency with the increase in the concentration of the inhibitor. In the present study, the displacement in the corrosion potential (E_{corr}) in the presence of the inhibitor is only around 10 mV than in its absence, which indicates that the inhibitor under consideration is a mixed type inhibitor. It means that the addition of the inhibitor reduced anodic dissolution of the metal as well as hydrogen evolution. Tafel slopes of both anodic and cathodic (β_a and β_c) reaction also varied on adding inhibitor to the solution indicating inhibitor worked as mixed type inhibitor and inhibiting action of the compound is merely blocking adsorption mechanism.²⁴

Electrochemical Impedance Spectroscopic Measurements (EIS)

The EIS provides a rapid and convenient way to investigate the performance of the organic-coated metals and has been widely used in corrosion studies. The corrosion of aluminum and mild steel in 1 M HCl was investigated by EIS method. The EIS data obtained are analysed using the equivalent circuit model (Fig. 3) which includes the solution resistance R_s which is placed in parallel to the charge transfer resistance R_t due to the charge transfer reaction and the double layer capacitance C_{dl} . The Nyquist plot for aluminum and mild steel in the absence and presence of nicotinic acid hydrazide at 303K are presented in Figs. 4 and 5 respectively.

Nyquist plots contain depressed semicircle with centre under real axis. The size of the semicircle increases with the inhibitor concentration, indicating the charge transfer process as the main controlling factor of the corrosion of aluminum.²⁵ It is clear from the figure that shapes of the impedance plots for inhibited specimen are not substantially different from those of uninhibited ones and the impedance of the inhibited solution increased with the increase in the concentration of the inhibitor but did not change the other aspect of the behavior.²⁶

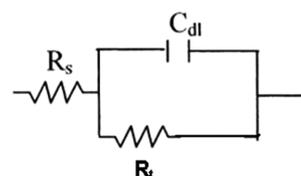


Figure 3. Electrical equivalent circuit used to fit the EIS data.

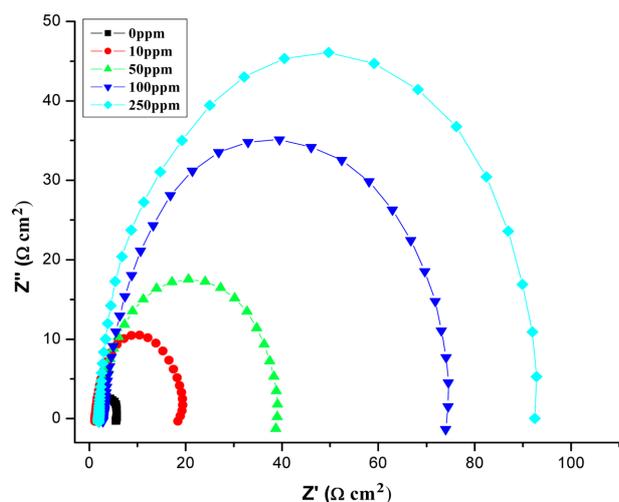


Figure 4. Nyquist plots for corrosion of aluminum in 1 M HCl solution at 303 K containing various concentrations of inhibitor.

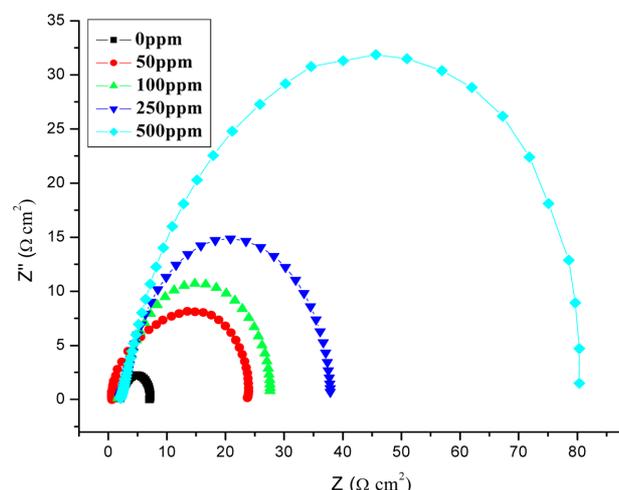


Figure 5. Nyquist plots for corrosion of mild steel in 1 M HCl solution at 303 K containing various concentrations of inhibitor.

Table 5. AC impedance data of Al in 1M HCl solution in the presence of inhibitor at 303 K

[Inhibitor]/ppm	R_t (Ωcm^2)	I.E (%)	C_{dl} (μFcm^2)
0	5.74	–	88.77
10	19.39	70.39	70.07
50	39.09	85.30	42.80
100	74.65	92.30	39.21
250	92.78	93.80	37.25

The experimental results of EIS measurements for the corrosion of aluminum and mild steel in 1 M HCl in the absence and presence of inhibitor are given in *Table 5* and *Table 6* respectively. It can be observed that charge transfer resistance (R_t) value increased with increase in the con-

Table 6. AC impedance data of mild steel in 1 M HCl solution in the presence of inhibitor at 303 K

[Inhibitor]/ppm	R_t (Ωcm^2)	I.E (%)	C_{dl} (μFcm^2)
0	7.17	–	318.4
50	23.96	70.07	228.3
100	27.78	74.19	218.4
250	37.96	81.11	210.8
500	80.06	91.04	138.5

centration of the inhibitor. On the other hand values of the capacitance of the interface (C_{dl}) started decreasing, with increase in inhibitor concentration, which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the inhibitor acts via adsorption at interface between metal and solution²⁷ and the decrease in the C_{dl} values is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the electrode surface, which decreases the extent of metal dissolution.²⁸

The inhibition efficiency is given by the following equation:²⁹

$$\text{I.E (\%)} = \frac{R_{t(\text{inhi})} - R_t}{R_{t(\text{inhi})}} \times 100 \quad (3)$$

where, R_t is charge transfer resistance without inhibitor, and $R_{t(\text{inhi})}$ is charge transfer resistance with inhibitor.

C_{dl} value is obtained from the Eq. (4):

$$C_{dl} = \frac{1}{2\pi f_{\text{max}} R_t} \quad (4)$$

where, f_{max} is the frequency at the top of the semicircle (where, Z'' is maximum).

Gravimetric Studies

The weight loss results of aluminum and mild steel in 1 M hydrochloric acid in the absence and presence of various concentrations of the inhibitor are summarized in *Table 7* and *Table 8* respectively. The inhibition efficiency³⁰ was calculated using equation (5).

Table 7. Corrosion parameters for aluminum after 4 hours of immersion in 1 M hydrochloric acid in the absence and presence of different concentrations of the inhibitor at 303 K

[Inhibitor]/ppm	Weight loss (mg cm^{-2})	I.E (%)
0	23.72	–
10	6.52	72.5
50	3.99	83.2
100	2.45	89.7
250	1.89	91.9

Table 8. Corrosion parameters for mild steel after 24 hours of immersion in 1 M hydrochloric acid in the absence and presence of different concentrations of the inhibitor at 303 K

[Inhibitor]/ppm	Weight loss (mg cm^{-2})	I.E (%)
0	127.52	–
50	48.10	62.22
100	37.96	70.22
250	30.27	76.26
500	21.85	82.86

$$\text{I.E (\%)} = \frac{W_2 - W_1}{W_2} \times 100 \quad (5)$$

where W_1 and W_2 are weight loss of aluminum or mild steel in the presence and absence of the inhibitor respectively. The inhibition efficiency increased with increase in the concentration of the inhibitor. Results obtained from polarization, EIS and weight loss measurements are in good agreement with each other.

Effect of Temperature

To elucidate the mechanism of inhibition and to determine the thermodynamic parameters of the corrosion process weight loss measurements were performed at various temperatures. The effect of temperature on the corrosion inhibition of aluminum and mild steel in the presence of the various concentrations of the inhibitor is graphically represented in *Fig. 6* and *Fig. 7* respectively. The inhibition efficiency decreased with increase in temperature indicating physisorption of the inhibitor on the metal surface. The reduced inhibition efficiencies of the inhibitors with increasing temperature may be due to the desorption of

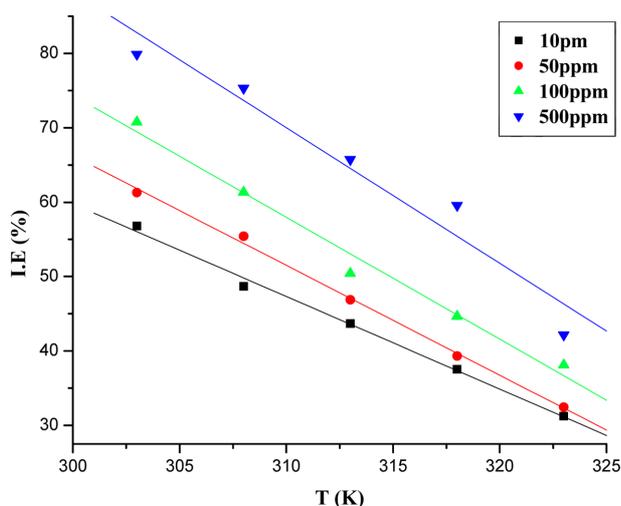


Figure 6. Plot of I. E vs T for corrosion of aluminium in 2 M HCl in the presence of different concentrations of inhibitor using weight loss method.

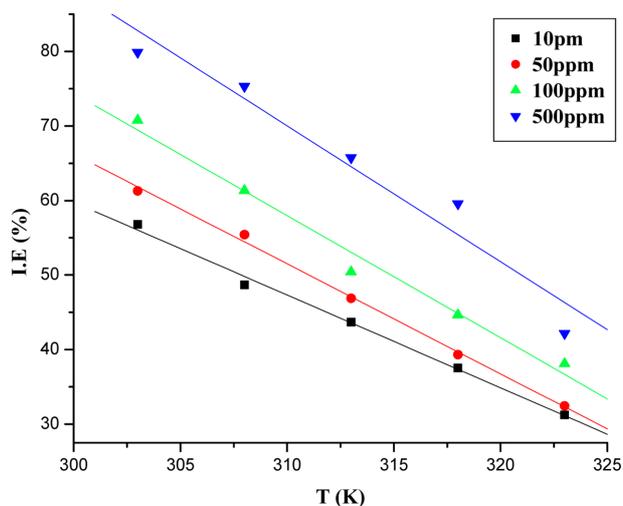


Figure 7. Plot of I.E vs T for corrosion of mild steel in 1 M HCl in the presence of different concentrations of inhibitor using weight loss method.

some adsorbed molecules from the surface of aluminum and mild steel at higher temperature. At higher temperature desorption predominates over adsorption. Therefore less number of inhibiting species are adsorbed on the surface of the aluminum and hence higher number H^+ ions attacks the surface of aluminum due to the availability of more active centers.

Surface Study by Optical Microscopy and Scanning Electron Microscopy

In order to evaluate the conditions of the metal surface in contact with acid solution in the absence and presence of inhibitor, microscopic analysis of the surface was carried out immediately after the corrosion tests using optical microscope and scanning electron microscope for aluminum and mild steel respectively. The aluminum and mild steel samples in 1 M HCl solution with and without optimal concentration of the inhibitor were subjected to analysis. Micrographs shown in *Fig. 8* and *Fig. 9* show that the surface corrosion of aluminum and mild steel decreased remarkably in the presence of the inhibitor. Inspection of the figures reveals that there is severe damage, clear pits and cavities on the surface of aluminum and mild steel in the absence of inhibitor than in its presence. This confirms that the metal surface is fully covered with adsorbed inhibitor molecules.

Mechanism of Corrosion Inhibition

Aluminum surface is positively charged at pH corresponding to 2.0 M HCl and 1.0 M HCl.³¹ Therefore, Cl anions of hydrochloric acid is specifically adsorbed on

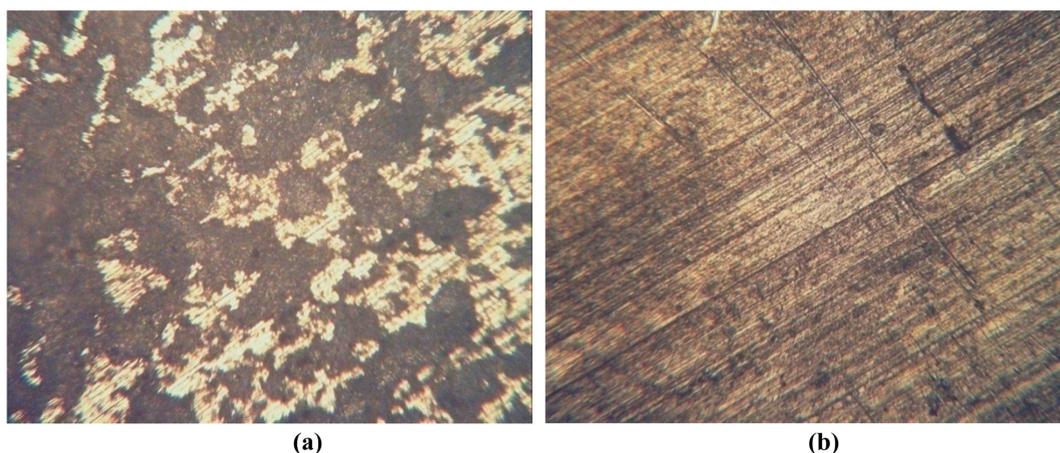


Figure 8. Optical micrographs of surface of aluminium in (a) only 1 M HCl (b) 1 M HCl with 250 ppm of the inhibitor.

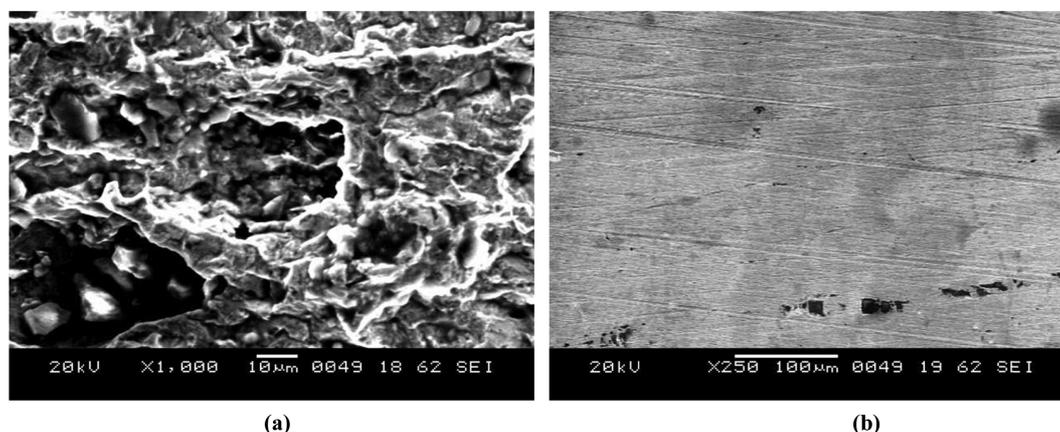


Figure 9. Scanning electron micrographs of surface of mild steel in (a) only 1 M HCl (b) 1 M HCl with 500 ppm of the inhibitor.

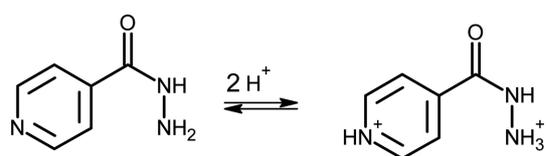


Figure 10. Protonation of nicotinic acid hydrazide in HCl (1 M/2 M) medium.

aluminum and mild steel surface, making it negatively charged as $(\text{AlCl}^-)_{\text{ads}}$ and $(\text{FeCl}^-)_{\text{ads}}$ species respectively.

In hydrochloric acid medium, studied inhibitor nicotinic acid hydrazide tend to exist in the form of cation, due to the protonation of nitrogen atom of pyridine ring. The protonation may also occur at nitrogen atom of the hydrazide group as shown in *Fig. 10*.

The protonated inhibitors may be adsorbed on the surface of the aluminum and mild steel through electrostatic interaction between positively charged inhibitor and negatively charged aluminum surface. The possible electrostatic interaction between the metal and the inhibitor is shown in *Fig. 11(a)*.

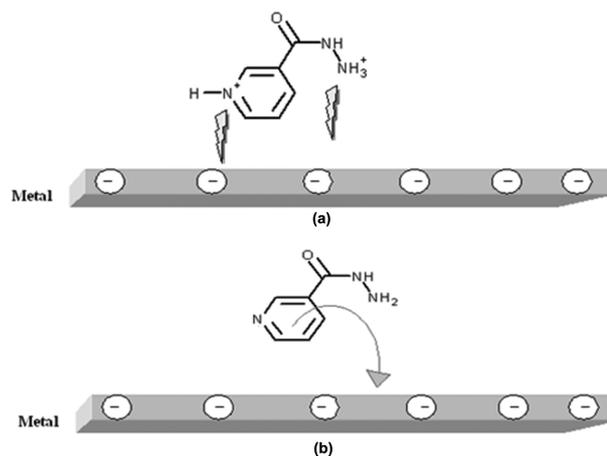


Figure 11. (a) Adsorption of nicotinic acid hydrazide on metal surface by electrostatic interaction, (b) Adsorption of nicotinic acid hydrazide on metal surface by π -interaction.

The adsorption of the inhibitor on the aluminum and mild steel surface may also be due to the interaction of the

π - electrons of the inhibitor with vacant orbitals of the aluminum and mild steel as shown in Fig. 11(b).

CONCLUSION

The weight loss, potentiodynamic polarization and impedance studies of the corrosion behaviour of aluminum and mild steel in the hydrochloric acid medium showed that nicotinic acid hydrazide acted as good inhibitor for the corrosion of aluminum and mild steel. The inhibition efficiency was more pronounced with the increase in the inhibitor concentration. Polarization studies suggested that the inhibitor inhibited both anodic and cathodic reactions of corrosion thus exhibited mixed type of inhibition. Inhibition efficiency for the corrosion of the aluminum and mild steel decreased with the increase in temperature in the studied temperature range indicating physisorption of the inhibitor on the metal surface.

Acknowledgments. The publication cost of this paper was supported by the Korean Chemical Society.

REFERENCES

- Jones, D. A. *Principles and Prevention of Corrosion*; Prentice Hall: New York, 1996.
- Jyotsna, S.; Pitre, K. S. *Bull. Electrochem.* **2004**, *20*, 309.
- Bereket, G.; Oğretir, C.; Yurt, A. *J. Mol. Struct.* **2001**, *571*, 139.
- Du, T.; Chen, J.; Cao, D. *J. Mater. Sci.* **2001**, *36*, 3903.
- Branzoi, V.; Florentian, G.; Florina, B. *Mater. Chem. Phys.* **2003**, *78*, 122.
- Obot, I. B.; Obi-Egbedi, N. O.; Umoren, S. A. *Corros. Sci.* **2009**, *51*, 1868.
- Zerfaoui, M.; Oudda, H.; Hammouti, B.; Kertit, S. *Prog. Org. Coat.* **2004**, *51*, 134.
- Mohamed Awad K., *J. Electroanal. Chem.* **2004**, *567*, 219.
- Ramesh, S. V.; Vasudeva, A. A. *Corros. Sci.* **2008**, *50*, 55.
- Bastidas, J. M.; Polo, J. L.; Cano, E. *J. Appl. Electrochem.* **2000**, *10*, 1173.
- Tamil, S. S.; Raman, V.; Rajendran, N. *J. Appl. Electrochem.* **2003**, *33*, 1175.
- Solmaz, R.; Kardas, G.; Culha, M.; Yazici, B.; Erbil, M. *Electrochim. Acta* **2008**, *53*, 5941.
- Schmitt, G. *Bri. Corros. J.* **1984**, *19*, 165.
- Hasanov, R.; Sadikoglu, M.; Bilgic, M. *Appl. Surf. Sci.* **2007**, *253*, 3913.
- Chetouani, A.; Hammouti, B.; Benhadda, T.; Daoudi, M. *Appl. Surf. Sci.* **2005**, *249*, 375.
- Yildirim, A.; Cetin, M. *Corros. Sci.* **2008**, *50*, 155.
- Obot, I. B.; Obi-Egbedi, N. O. *Colloids Surf. A Physicochem. Eng. Aspects* **2008**, *330*, 207.
- Khaled, K. F.; Al-Qahtani, M. M. *Mater. Chem. Phys.* **2009**, *113*, 150.
- Ma, H.; Song, T.; Sun, H.; Li, X. *Thin Solid Films* **2008**, *516*, 1020.
- Ju, H.; Kai, Z. P.; Li, Y. *Corros. Sci.* **2008**, *50*, 865.
- Ebenso, E. E. *Mater. Chem. Phys.* **2003**, *79*, 58.
- Emrgul, K. C.; Akay, A. A.; Atakol, O. *Mater. Chem. Phys.* **2005**, *93*, 325.
- Zerga, B.; Attayibat, A.; Sfaira, M.; Taleb, M.; Hammouti, B.; Ebn, T. M.; Radi, S.; Rais, Z. *J. Appl. Electrochem.* **2010**, *40*, 1575.
- Xiang-Hong, L.; Shu-Dhuan, D.; Hui, F. *J. Appl. Electrochem.* **2010**, *40*, 1641.
- Sekin, I.; Sabongi, M.; Hagiuda, H.; Oshibe, T.; Yuasa, M.; Imahc, T.; Shibata, Y.; Wake, T. *J. Electrochem. Soc.* **1992**, *139*, 3167.
- Poornima, T.; Jagannath, N.; Nityananda, S. A., *J. Appl. Electrochem.* **2010**, *41*, 223.
- Aljourani, J.; Raeissi, K.; Golozar, M. A. *Corros. Sci.* **2009**, *51*, 1836.
- Khaled, K. F. *Electrochim. Acta.* **2003**, *48*, 2493.
- Cruz, J.; Martinez, R.; Genesca, J.; Garcia-Ochoa, E. *J. Electroanal. Chem.* **2004**, *566*, 111.
- QiBo, Z.; YiXin, H. *Mater. Chem. Phys.* **2010**, *119*, 57; Khaled K. F. *Corros. Sci.* **2010**, *52*, 2905.