Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(2):388-396

Inhibitive Properties of Nitrogen Containing Heterocyclic Compounds over Aluminium Alloys in Organic Acid Environment

Arvnabh Mishra*, D. R. Godhani# and Anil Sanghani#

**Department of Chemistry, ARIBAS, New Vallabh Vidyanagar, Anand*
#Department of Chemistry, Bhavnagar University, Bhavnagar

ABSTRACT

The effects of Pyridine, Pyrimidine, 2-Picoline, Quinoline, 2:6-Lutidine and Isoquinoline on the corrosion inhibition of 1060 aluminium in 0.1N concentration of trichloroacetic acid at varying temperature of 30°C and 40°C are investigated by weight loss method in conjunction to the concentration of corroding media, period of immersion of Aluminium alloy grade 1060 at the temperature 30℃ with respect to the concentration of inhibitor and activation energy and adsorption isotherms are plotted to elucidate the mechanism of adsorption of inhibitor on surface of alloy in that support corrosion potential and its trends are observed cathodic in nature.

Keywords: Aluminium alloy 1060, Tri-chloroacetic Acid, weight loss, adsorption, 2:6-Lutidine, Isoquinoline, activation energy

INTRODUCTION

Nitrogen-containing organic compounds, such as amines and diamine derivatives on the corrosion for many metals in acidic solutions offer good protection of metallic materials [1,2]. The behaviour of some pyridine derivatives towards the inhibition of corrosion has been investigated for 1060 aluminium alloys in 0.1N trichloroacetic acid at 30° and 40° C.

The concentration of trichloroacetic acid was kept steady. The concentration of inhibitors was varied from 6 to 15 ppm. Temperatures of the systems were also changed from 30°C to 40°C for each of the alloys studied. Loss in weight was recorded for 24 hours immersion period, to calculate the inhibition efficiencies of the inhibitors.

EXPERIMENTAL SECTION

For weight loss studies, Aluminium alloy coupons were mechanically polished with different grade emery papers and degreased with acetone, washed thoroughly with conductivity water and finally dried in air[3]. Coupons were weighed and suspended vertically in aerated unstirred 0.1 N and 0.5 N Trichloroacetic acid (150 ml) with and without inhibitor for 24 h. Coupons were removed from solution and cleaned by brushing under running tap water to remove corrosion products, dried and reweighed to determine weight loss.

In each case, triplicate experiments were performed and inhibition efficiency (IE) was determined as:
IE = 100 x (Wo – Wi) /Wo …(1)

Where Wo and Wi are weight losses in uninhibited and inhibited corroding solutions respectively. Expression, □=1-(Wi/Wo) was used to determine degree of surface coverage (□). Corrosion rate (mg/cm2/h) was also calculated.

Potentiostatic polarization experiments [4] were carried out using a Wenking Potentiostate. The working electrodes for polarization studies were flag-shaped, 2 cm^2, with a side tag of length 40 mm. Part of the tag was blocked off with paraffin wax leaving the upper part bare to make electrical contact. The experiments were carried out in a 200 ml pyrex glass cell containing 100 ml test solution of 0.1 N chloro substituted acetic acids, with and without inhibitors at which maximum efficiency was observed. Platinized platinum foil was used as the auxiliary electrode. Standard calomel electrode with Luggin capillary was used for the measurement of electrode potentials.

RESULTS AND DISCUSSION

Results are summarized in Tables-1 to 3 and Figures-1 to 3.

In the Table-1 the effects of the concentration of pyridine, pyrimidine, quinoline, isoquinoline, 2:4 lutadine, 2-picoline on corrosion of the aluminium alloys at 30° and 40° C and at an exposure period of 24 hours have been recorded. Starting from a very low concentration of the inhibitors (6 ppm) it was increased upto (15 ppm). The data in the Table shows that at all the concentrations pyridine is the poorest inhibitor among all the studied compounds. At the concentration of 6 ppm, Pyrimidine has a little effect on the corrosion of all the investigated alloys.

As the concentration of the inhibitor was 7.5 times increased the inhibition efficiency increases by approximately 55 percent. It is seen from the table that pyrimidine is more efficient than pyridine.

Table-1bring out the fact that 2-picoline shows the inhibition efficiency of the order of 21 percent for 1060, at the concentration of 8 ppm. The efficiency of the inhibitors increase with their concentrations and at 15 ppm concentration, the observed efficiency become about two times more than that of the pyridine found at this concentration and maximum protection is observed. At all concentrations of quinoline protection was greater than pyridine has been found. 2:4-lutadine has shown an appreciable improvement in the inhibition efficiencies even at lower concentration[5]. Like other inhibitors of the group, this compound also shows the greatest protection.

It was found that the inhibition efficiencies of the inhibitors decrease when the temperature was raised from 30°C to 40°C [Table-1] and the increase in the temperature does not change the nature of action discussed above at 30°C. The concentration required for the maximum inhibition of the compounds, however, remains the same at the two temperatures [15ppm] for all the compounds. The extent of inhibition decreases with increase in temperature because of desorption of the inhibitor which exposes greater surface area of the metal to the corrosive medium.[6] Putilova compares such type of inhibitors showing poorer inhibition at higher temperatures with unstable catalyst poisons the adsorption of which fall off appreciably with rise in temperature and hence a decrease in efficiency results[7,8].

The percentage inhibition of the inhibitors at the concentration of 15 ppm was determined at different periods of the immersion for all the three alloys. The corresponding plots for the alloys exhibiting the variation of the percentage inhibition with the immersion period have been shown in Figures-1.

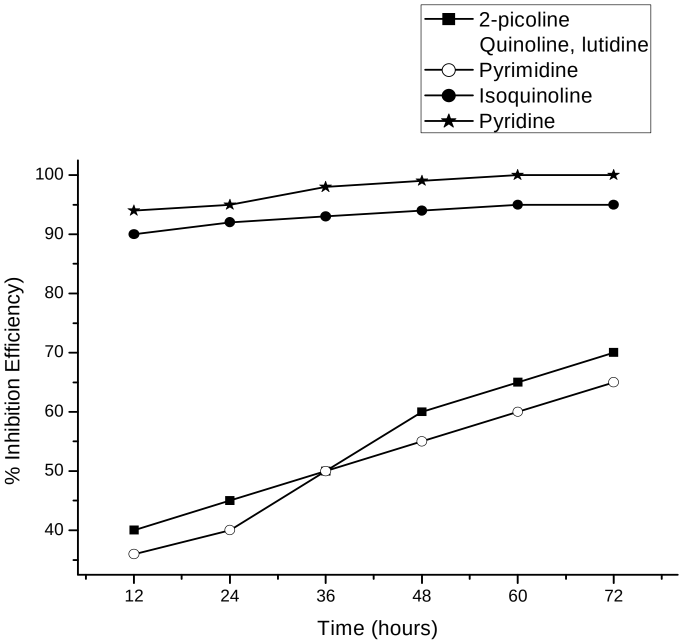

Figure-1: Variation of percentage inhibition efficiency with immersion period at 30^{0}C for 1060 Alluminium alloy

The temperature was kept constant at 30°C. It is inferred from the Figure that pyridine and pyrimidine show strengthening in the inhibition (Efficiencies with the passage of time up to a period of 48 hours after which the efficiencies remains almost constant. A marked improvement in the inhibition efficiencies of the other inhibitors has also been observed although to a lesser extent.

It can be seen from the Figures that at an exposure period of 72 hours pyridine and pyrimidine show an inhibition of the order of 65 and 69 percent for 1060 alloys. The strengthening in inhibition may be due to increase in extent of adsorption with the passage of time [9].

Table-1: Loss in weight (m) and percentage inhibition efficiencies (E) surface coverage (□) and rate of 1060 alloy in the presence of different concentrations of the inhibitors at 30^0C and 40^0C

Concentration	**At 30^0C**				**At 40^0C**			
ppm	**weight loss m (mg)**	**Efficiency (E)**	**Surface coverage (□)**	**Rate mg/mm^2/hr**	**weight loss m (mg)**	**Efficiency (E)**	**Surface coverage (□)**	**Rate mg/mm^2/hr**
Uninhibited Solution	**174**				**238**			
Pyridine								
6	162.8	6	0.06	0.09	224.75	6	0.06	0.12
8	150.61	13	0.13	0.08	216.7	9	0.09	0.12
10	128.12	26	0.26	0.07	183.45	23	0.23	0.10
15	78.8	55	0.55	0.04	116.05	51	0.51	0.06
Pyrimidine								
6	131.96	24	0.24	0.07	191.74	19	0.19	0.10
8	123.85	29	0.29	0.07	173.15	27	0.27	0.09
10	115	34	0.34	0.06	163.22	31	0.31	0.09
15	72.84	58	0.58	0.04	110.1	54	0.54	0.06
2-Picoline								
6	158.62	9	0.09	0.09	223.00	6	0.06	0.12
8	137.27	21	0.21	0.08	198.42	17	0.17	0.11
10	99.83	43	0.43	0.05	149.95	37	0.37	0.08
15	5	97	0.97	0.00	29.80	87	0.87	0.02
Quinoline								
6	130.28	25	0.25	0.07	184.67	22	0.22	0.10
8	110.2	37	0.37	0.06	152.95	36	0.36	0.08
10	62.53	64	0.64	0.03	100.13	58	0.58	0.05
15	5	97	0.97	0.00	21.07	91	0.91	0.01
2,6 lutidine								
6	128.23	26	0.26	0.07	169.98	29	0.29	0.09
8	96.54	45	0.45	0.05	141.35	41	0.41	0.08
10	49.08	72	0.72	0.03	98.76	59	0.59	0.05
15	1.12	99	0.99	0.00	8.23	97	0.97	0.00
Isoquinoline								
6	119.2	31	0.31	0.07	168.56	29	0.29	0.09
8	90.12	48	0.48	0.05	146.89	38	0.38	0.08
10	29.67	83	0.83	0.02	62.73	74	0.74	0.03
15	2.94	98	0.98	0.00	18.46	92	0.92	0.01

In order to confirm whether the inhibitors obey the adsorption isotherm equation or not, the degree of the surface covered by them (i.e. the percentage inhibition efficiencies) was kept in the various adsorption isotherms. At any instant a fraction θ of the metal surface is covered by the inhibitor molecules and the uncovered fraction (1- θ) reacts with acid as it does in the absence of inhibitor. The surface coverage increases thereby increasing the percentage inhibition. To examine the adsorption behaviour of the inhibitor, the data were fitted to the various isotherms. A plot of log θ/(1-θ) versus Log C was a straight line supporting the monolayer adsorption of the inhibitor. It is clear from the Figures that the plots are linear with slightly scattered points in few cases. This deviation from the linearity may be due to some experimental error or slight in homogeneity of the metal surface.

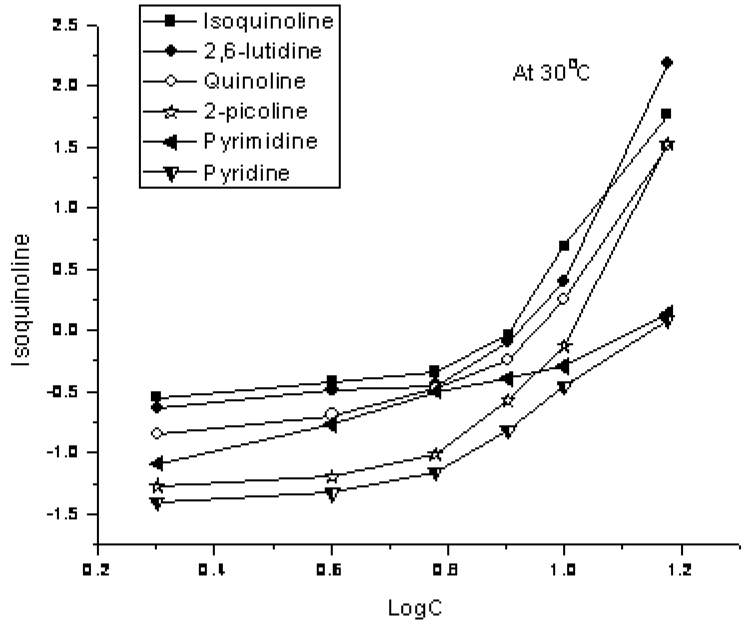

Figure-2: Langmuir adsorption plots for 1060 aluminium alloy in presence of inhibitors at 30^{0}C

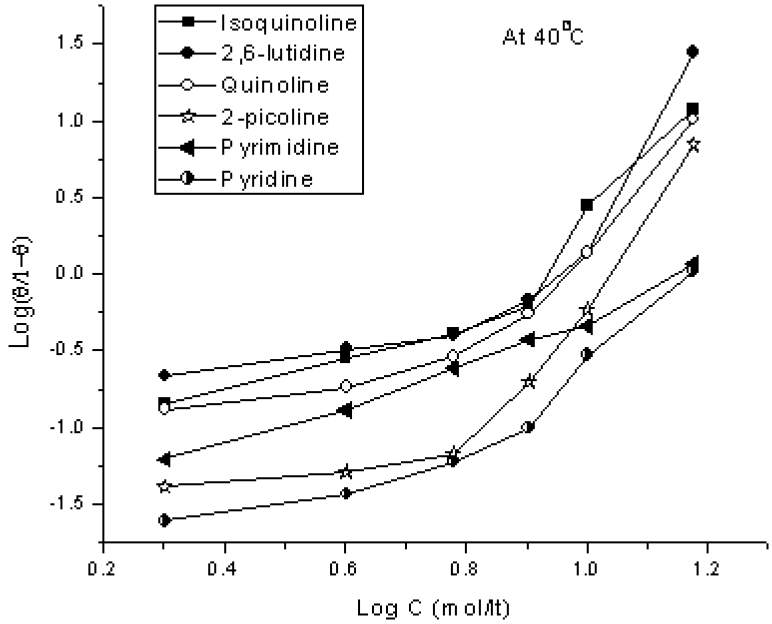

Figure-3: Langmuir adsorption plots for 1060 aluminium alloy in presence of inhibitors at 40^{0}C

Table-2: Percentage inhibition efficiency (E), Energy of activation (E_a), Heat of adsorption ($-Q_{ads}$), and Free energy (ΔG) for 1060 Aluminium in 0.1N Trichloroaceetic acid

Temperature range 30^0C - 40^0C Immersion period: 24 Hrs

Inhibitors and concentrations (ml/lt)	**Efficiency (E)**		**Ea KJ/mole**	**Qads Kj/mole**	**Free Energy K J/mol**	
	30^0C	**40^0C**			**30^0C**	**40^0C**
Uninhibited			**25.17**			
Pyridine						
6	6	6	27.27	-6.13	-9.91	-9.83
8	13	9	30.55	-18.15	-11.23	-10.41
10	26	23	30.08	-7.38	-12.78	-12.71
15	55	51	32.13	-5.54	-14.82	-14.94
Pyrimidine						
6	24	19	29.38	-11.03	-13.80	-13.53
8	29	27	26.26	-3.10	-13.68	-13.93
10	34	31	27.44	-4.49	-13.71	-13.87
15	58	54	32.31	-7.09	-15.20	-15.24
2-Picoline						
6	9	6	26.98	-14.51	-11.18	-10.60
8	21	17	29.14	-11.66	-13.01	-12.68
10	43	37	32.08	-9.34	-15.03	-14.91
15	97	87	140.53	-62.57	-23.62	-20.30
	Quinoline					
6	25	22	27.56	-5.96	-15.13	-15.24
8	37	36	25.80	-1.60	-15.78	-16.20
10	64	58	37.04	-10.25	-18.05	-17.98
15	97	91	113.52	-47.18	-24.44	-22.16
	2,6 lutidine					
6	26	29	21.22	4.54	-14.82	-15.61
8	45	41	29.09	-6.35	-16.14	-16.25
10	72	59	54.19	-23.44	-18.48	-17.55
15	99	97	155.98	-67.87	-27.80	-24.27
	Isoquinoline					
6	31	29	28.28	-4.35	-15.93	-16.17
8	48	38	39.52	-16.11	-16.98	-16.48
10	83	74	59.84	-22.01	-20.58	-19.82
15	98	92	145.50	-63.01	-25.81	-22.53

It is further seen from Figures that in almost all of the corrosion inhibitors except pyrimidine showing linearity. The observed slopes have been found equal to unit in any case, as is expected by Langmuir in his adsorption isotherm equation. The reason for the departure from the ideal behaviour may be explained in terms of interaction between the adsorbed inhibitor species on the metallic surface. There was a possibility that inhibitor molecules adsorbed at different sites (anodic and cathodic) may interact. There was also another possibility of interaction between already adsorbed molecules and those being adsorbed. Due to these interactions, the heat of adsorption of the inhibitors was affected. However, Langmuir in the derivation of adsorption equation did not consider this interaction factor. It seems that the difference in the heat of adsorption due to these interactions was a cause for deviation from the ideal behaviour of the isotherm. [10,11].

From the Table-2 the values of Ea and Gads are given.

Activation energy, E_a (KJ/mol) at 303K and 313K for all concentration of inhibitor was calculated using Arrhenius equation

$$k = A\, e^{-Ea/RT} \qquad \text{………………. (2)}$$

where k is specific first order rate constant (h^{-1}), *A* is Arrhenius frequency factor, *R* is universal gas constant (8.314 J/mol/K) and *T* is temperature in K. Taking natural logarithm of Eq. (2) and after rearrangement gives

$$Ea = [19.14\, T_1T_2\, (\log k_{313} - \log k_{303}\,]\, /\, 1000\, (T_2 - T_1) \qquad \text{…(3)}$$

T_2 represents 313 K while T_1 represents 303 K with the corresponding rate constants k_{313} and k_{303}.

The values of activation energy were found higher at inhibited system over the uninhibited system. Lower activation energy means a fast reaction and high activation energy means a slow reaction. High activation energy corresponds to a reaction rate that is very sensitive to temperature. Conversely small activation energy indicates a reaction rate that varies only slightly with temperature. If a reaction has zero activation energy its rate is independent of temperature

From the value of Q_A given in Table-2, it is assumed the inhibitor is adsorbed on the metal surface in the form of monolayer film, covering at any instant fraction θ, of the metal surface in a uniform random manner, than the heat of adsorption Q_A, of the inhibitor can be calculated with the help of the equation[3]:

$$Q_A = 2.303 \times \left(\frac{T_1 \times T_2}{T_2 - T_1} \right)\left(\text{Log}\,\frac{Wo - Wi}{Wi} - \text{Log}\,\frac{Wo - Wi}{Wi} \right) \text{……….. (4)}$$

Where,
W_o = weight losses in uninhibited acid and Wi = weight losses in inhibited acid solutions by the inhibitor at Kelvin temperatures T_1 and T_2 respectively.

The values of the free energy ΔG° less than -40 KJ/mol (-9.56 Kcal/mol) indicated that the tested inhibitors were physically adsorbed on the metal surface.[8,10] The low and negative value of ΔG° indicates the spontaneous adsorption of inhibitor on the surface of alloy.[12-14] It was also found that values of activation energy of the inhibited systems were lower than that of uninhibited system. Putilova[7] has indicated that this type of inhibitor is effective at higher temperatures. The values of adsorption ΔG^o were calculated from the equation:

$$\Delta G_0 = 2.303 \times R \times T\ (\text{Log}\, C_{inh} - \text{Log}\,\frac{Wo - Wi}{Wi} - 1.75 \qquad \text{---- (5)}$$

Where, R = Constant (1.987), T= Temperature in Kelvin
C= Concentration of inhibitor in mole/L

Steady state corrosion potential

Steady state corrosion potential exhibited by the inhibiting compounds at their optimum concentrations at 30°C has been summarized in Table-3. It was interesting to note that corrosion potential of the inhibitors move towards active direction with respect to uninhibited electrodes reaction, as the effectiveness of the inhibitors increases. It was clear from the Table that on addition of pyridine compounds, potential slightly changes.

On addition of 2-picoline corrosion potential shifts still more towards the active direction. Order of shifts of the active direction was found greatest in isoquinoline followed by 2:4 lutidiene.

The shifts of corrosion potentials in the active direction indicate that inhibitors were cathodic in nature [15, 16, 17].

Table-3: Steady state corrosion potential (E_{corr}) of different alloys in the presence of 15 ppm of the inhibitors at 30^0C

Inhibitors	**Steady state corrosion potential (mV)**
	1060
Uninhibited solution	-0.510
Pyridine	-0.520
Pyrimidine	-0.525
2-Picoline	-0.530
Quinoline	-0.550
2:6-Lutidine	-0.555
Isoquinoline	-0.570

CONCLUSION

It is observed that pyridine and pyrimidine show poorer performance than other inhibitors. Maximum inhibition efficiency has been recorded at 15 ml/l concentration of inhibitors. There were found a direct relation between inhibition efficiency and concentration of inhibitors. Inhibitors are also observed cathodic in nature.

REFERENCES

[1] A Mishra, D B Sanja, A M Sanghani & D R Godhani, *Int. J. Chem. Sci.*: 6(2), **2008**, (665-675)
[2] Dr D. R. Godhani, A Mishra, Anil Sanghani, Divyesh Sanja, *TAJEC* 3(1&2), **2008**, (36)
[3] Champion F A, *Corrosion Testing Procedures* (Champman & Hall, London) **1952**, 187-189.
[4] H. C. Gatos, *Corrosion*, 12 **(1956)** 23
[5] Dongshe Zhang, , Lidong Li, Lixin Cao, Neifen Yang and Chubao Huang *Corrosion Science* Volume 43, Issue 9, **(2001)** 1627.
[6] J.R.Becker, Corrosion and Scale Handbook; **(1998)** 329.
[7] O.K.Abiola,N.C.Oforka JCSE,J.corros.Sci.Eng.3,21**,(2002).**
[8] E.E.Ebenso *Jour.Nig.Corrosion*.1,(1)**,(1998)**.
[9] U.J.Ekpe,U.J.Ibok,B.I.Ita,O.E.Offiong, E.E.Ebenso Mater. Chem. Phy. 40, 87, **(1995).**
[10] E.E.Ebenso,P.C.Okafor,O.E.Offiong,B.I.Ita,U.J.Ibok,U.J.Ekpe *Bull. Electrochem*. 17, 259, **(2001).**
[11] I.N. Putilova, V.P. Barannik and S.A. Balezin, "*Metallic Corrosion Inhibitors*", Pergaman Press, Oxford, **(1960)** 30.

[12] N. Hackerman and A.C. Makrides, *Indian Eng. Chem*. 46 **(1954)** 523.
[13] Kliskic M., Radosevic J, and Gudic S.; *Journal of applied electrochemistry*; Vol.-27 **(1997)** 947
[14] S.A. Abd El-Maksoud and A.S. Fouda, *Materials Chemistry and Physics Elsevier* Vol-93, Issue-1**(2005**) 85
[15] H.S. Awad,*Journal of Anti-Corrosion Methods and Materials*, Vol-53 issue-2 **(2006)** 110
[16] M. Lashkari and M. R. Arshadi , *Chemical Physics*;Vol-299, Issue-1, **(2004)** 131
[17] A.O. James, N.C. Oforka, and O.K. Abiola, *The Journal of Corrosion Science and Engineering*; 21 Vol-7 Preprint 21**(2005)**