ejbps, 2015, Volume 2, Issue 2,143-154. **Research Article** **SJIF Impact Factor: 2.062**

EUROPEAN JOURNAL OF BIOMEDICAL
AND
PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 2
Issue: 2
143-154
Year: 2015

INHIBITION EFFICIENCY OF THIOUREA AND ISOMETHYLTHIOUREA ON ALUMINUM CORROSION IN TRICHLOROACETIC ACID

P S Desai*

Department of Chemistry, Arts, Science and Commerce College Kholwad, Kamrej Char Rrasta,
Surat- 394185, Gujarat, India.

Article Received on 04/01/2015 **Article Revised on 24/01/2015** **Article Accepted on 16/02/2015**

***Correspondence for Author**
Dr. Desai Piyush
Department of Chemistry,
Arts, Science and Commerce
College Kholwad, Kamrej
Char Rrasta, Surat, Gujarat,
India.

ABSTRACT

Thiourea and Isomethylthiourea were studied as a corrosion inhibitor for aluminum in trichloroacetic acid (TCA) solution. The inhibition efficiency depended on the concentration of acid and the inhibitor. Inhibition efficiency of TCA solutions increased with the concentration of Thiourea And Isomethylthiourea, but decreased with rise in temperature, this corresponded to surface coverage of the metal by the inhibitor. The degrees of surface coverage, θ, were calculated and found to increase with the inhibitor concentration. The results show also that, the inhibitors were adsorbed on the aluminum surface according to Langmuir adsorption isotherm. Polarization study reveals that the inhibitors function as a little anodic, but significant cathodic inhibitor.

KEYWORDS: Corrosion, Aluminum, Trichloroacetic acid, Thiourea and Isomethylthiourea, Adsorption.

INTRODUCTION

Corrosion process degrades the metallic properties of metal/alloys and renders them to be rejected from the special structures of industrial importance. Since metal have a high electric conductivity, their corrosion is usually of an electrochemical in nature. Aluminum and its alloy show high resistivity towards a wide variety of corrosive environments. This is may be due to the formation as protective, tightly adherent and at times invisible oxide film on the metal surface. The film is generally stable in solutions of pH 4.5- 8.5.[1] Acid solutions mainly HCl and H_2SO_4 are generally used for the removal of undesirable scale and rust in several industrial processes. For this reason some sorts of inhibitors are generally used to control metal dissolution as well as acid consumption.[2]

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. Most of the well-known acid inhibitors are organic compounds containing polar nitrogen, oxygen or sulfur atoms in a conjugated system have particularly been reported to exhibit corrosion inhibiting efficacy.[3-8] The inhibition efficiency strongly depends on the structure and chemical properties of the layers that are formed under the particular experimental condition. Heteroatoms containing organic compounds has been used extensively as corrosion inhibitors for the corrosion of metals in acid solutions. At the same time, there is very little information about the inhibition of aluminum corrosion in TCA solutions using such organic compounds. Some researcher used amino acetanilides [9], ansidines [10,11] and Nitro aniline [12] as corrosion inhibitors for aluminum corrosion in acid solution. Desai et al.[13] studied the corrosion inhibition behavior of aluminium in TCA in the absence and presence of Phenyl thiourea used as corrosion inhibitors by weight loss and Polarization technique. Therefore, the main aim of the present work is to investigate the effect of Thiourea and Isomethyl thiourea on the corrosion of aluminum in TCA solution, using gravimetric and polarization technique.

EXPERIMENTAL PROCEDURE

Aluminum sheets of the 2S, type aluminum (Al = 98.02%; Mg = 0.37%; Si = 0.49%; Fe = 0.68%; Mn = 0.16; and Cu = 0.082%) was used in this study. Each sheet, which was 0.18 cm in thickness, was mechanically press-cut into coupons of dimension 2 x 5 cm with small hole of about 5 mm diameter near the upper edge. These coupons were used in the “as cut” condition, inhibition efficiency without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use. All chemicals and reagents used were of analytical grade and used as source without further purification. The aggressive media were, respectively, 0.01, 0.05 and 0.1 M TCA solutions. Thiourea and its derivatives were used as inhibitor in the concentration range 5 to 20mM.

The test specimens were immersed in 0.01, 0.05 and 0.1 M TCA solution with and without inhibitors. Only one specimen was suspended by a glass hook, in each beaker containing 230 ml of the test solution and was open to air at room temperature for 24 h duration. After the test, the specimens were cleaned with chromic-phosphate mixture solution.[14] Triplicate experiments were performed in each case and the mean values of the weight loss data are presented in Table 1.

To study the effect of temperature on corrosion rate, the specimen was immersed in 230 ml in 0.05 M TCA, with thiourea as inhibitor concentration 5, 10, 15, and 20mM at solution temperatures of 313, 323 and 333 K for a period of 2 h. To study the effect of temperature, thermostat assembly with an accuracy of ± 0.5^{oaks} was used. Wesley **[15]** and ASTM **[16]** pointed out that thermostatic controls to within ± 1^{o}C usually are considered satisfactory. Inhibition efficiency (η %), energy of activation (E_a), heat of adsorption (Q_{ads}) free energy of adsorption (ΔG^0_{ads}), enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated and shown in Table 2&3.

For polarization study, metal specimens of rectangular design having an area of 0.02585 dm^2 are exposed to corrosive solutions. Aluminum alloy is used as a working electrode, Ag/AgCl is used as reference electrode and the auxiliary platinum electrode was placed in a 100 ml corrosive media through which external current was supplied automatically from the computerized polarization instrument. The change in potential was measured by potentiostate/galvanostate (Auto lab polarization Model-273). Galvanostatic polarization has been taken with and without inhibitors in 0.01 M TCA. It curves shows polarization of both the anodes and cathodes.

RESULTS AND DISCUSSION

The results are presented in Tables 1 to 4 and Figures 1 to 2. To assess the effect of corrosion of aluminum in TCA, thiourea and its derivatives is used as inhibitors.

Specific conductivity of 0.01, 0.05 and 0.1 M acid concentration was found to be 3.25×10^{-3}, 16.79×10^{-3} and 30.30×10^{-3} milimohs / cm respectively. This suggests that specific conductivity increase with increase of acid concentration. The addition of inhibitors decreases the specific conductivity. Specific conductivity for Thiourea and Isomethylthiourea at 5mM inhibitor concentration in 0.01 M acid concentration is 3.27×10^{-3} and 3.24×10^{-3} milimohs / cm respectively.

The corrosion rate of aluminum metal in TCA was increased with the acid concentration which was shown in Table 1. The inhibition efficiency (η %) and degree of surface coverage

(θ) at each concentration of Thiourea and Isomethylthiourea were calculated by comparing the corrosion loss in the absence (W_u) and presence of inhibitors (W_i) using the relationships:

$$\eta\% = \left(\frac{Wu - Wi}{Wi}\right) X100 \qquad (1)$$

$$\theta = \left(\frac{Wu - Wi}{Wi}\right) \qquad (2)$$

Table :1 Effect of acid concentration on corrosion loss (CL) and inhibition efficiency (η %) of aluminum in TCA.

Temp. 301 ± 1 K, Immersion Period: 24 h, Effective Specimen area: 0.2414 dm^2

Inhibitor	I.C. mM	Acid Concentration					
		0.01 M		0.05 M		0.1 M	
		C. L. mg / dm^2	I. E %	C. L. mg / dm^2	I. E %	C. L. mg / dm^2	I. E %
I	II	III	IV	V	VI	VII	VII
Blank	-	118.88	-	1189.3	-	2452.09	-
Thiourea	5	38.94	67.24	669.01	43.75	1731.67	29.38
	10	36.45	69.34	642.92	45.94	1714.99	30.06
	15	26.45	77.75	566.28	52.39	1669.87	31.90
	20	6.63	94.42	378.20	68.20	1623.77	33.78
Isomethyl thiourea	5	77.41	34.89	793.74	33.26	1743.44	28.90
	10	65.81	44.64	713.58	40.00	1722.59	29.75
	15	65.81	44.64	698.95	41.23	1657.86	32.39
	20	60.84	48.82	680.28	42.80	1619.61	33.95

As a constant inhibitor concentration, the inhibition efficiency decreases with the increase in acid concentration. At 20 mM inhibitor concentration, the inhibition efficiency of thiourea is 94.42, 68.20 and 33.78 % with respect to 0.01, 0.05 and 0.1 M acid concentration respectively. At a constant acid concentration, the inhibition efficiency of the thiourea and its derivative increases with the inhibitor concentration, e.g. Isomethyl thiourea in 0.01 M TCA the inhibition efficiency was found to be 67.24, 69.34, 77.75 and 94.42 % with respect to 5, 10, 15 and 20mM inhibitor concentration respectively (Table 1).

The temperature has significant influence on a metal corrosion rates. The effect of change in temperature on the corrosion rates of aluminum in 0.05 M TCA, the corrosion of aluminum was increased with rising temperatures. Corrosion rate was measured in 0.05 M TCA containing 5, 10, 15 and 20mM inhibitor concentration at a solution temperature of 313, 323 and 333 K for an immersion period of 2h. In 0.05 M TCA solution with 20mM inhibitor concentration, the inhibition efficiency for Isomethyl thiourea was decreased corresponds to 39.15, 38.13 and 32.04 % in 313, 323 and 333 K respectively (Table 2).

Table 2: Effect of temperature on corrosion rate (CL), inhibitive efficiency (η %), for aluminum in 0.05M TCA contain inhibitors at different inhibitor concentration.

Immersion Period : 2h, Effective Specimen area : 0.2488 dm²

	Inhibitor Cincentra tion	Temperature K					
		313		323		333	
		C. R. mg/ dm²	I. E %	C. R. mg/ dm²	I. E %	C. R. mg/ dm²	I. E %
Blank	-	194.70	-	310.68	-	426.68	-
Thiourea	5	130.10	33.18	219.55	29.33	372.83	12.62
	10	119.88	38.43	208.75	32.81	356.45	16.46
	15	98.27	49.53	171.90	44.67	328.84	22.93
	20	60.45	68.95	132.94	57.21	302.40	29.12
Isomethyl thiourea	5	128.02	34.25	213.19	31.38	302.40	29.12
	10	126.21	35.18	206.91	33.40	297.91	30.18
	15	122.33	37.17	200.20	35.56	293.68	31.17
	20	118.48	39.15	192.22	38.13	289.98	32.04

In the present study general type of corrosion occurs predominately and less pitting. Plotting of log θ/1-θ versus log C (mM), straight lines were obtained, indicating that the adsorption of the added inhibitors followed the Langmuir adsorption isotherm (Figure 1a & 1b). Therefore, adsorption of these compounds is assumed to occur uniformly over the metal surface.

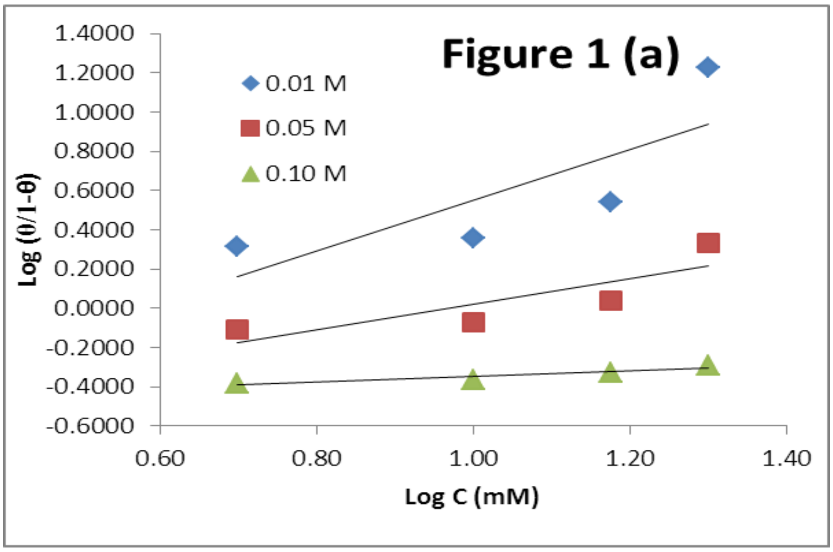


Figure 1(a): Plot of log (θ / 1-θ) Versus log C(M) for Thiourea.

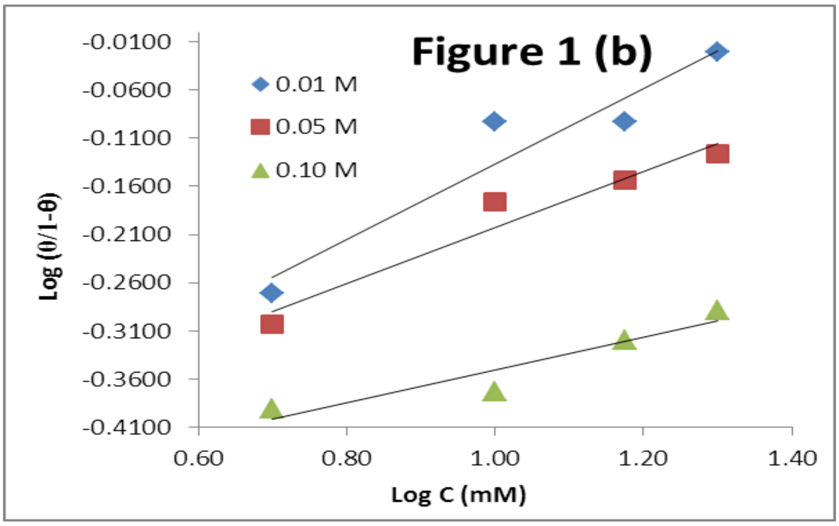


Figure 1(b): Plot of log (θ / 1-θ) Versus log C(M) for Isomethylthiourea.

The values of the free energy of adsorption (ΔG^0_{ads}) were calculated with slope of the following equation.[17]

$$LogC = L\,og\left(\frac{\theta}{1-\theta}\right) - LogB \qquad (3)$$

Where $LogB = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT}\right)$ and C is the inhibitor concentration. The mean ΔG^0_a values are negative almost in all cases and lie in the range of -19.76 to -22.90 kJ. mol^{-1} shown in Table 3. The most efficient inhibitor shows more negative ΔG^0_a value. This suggests that they be strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji.[18] The values of heat of adsorption (Q_{ads}) were calculated by the following equation.

$$Q_{ads} = 2.303R\left[Log\left(\frac{\theta_2}{1-\theta_2}\right) - Log\left(\frac{\theta_1}{1-\theta_1}\right)\right] X \left[\left(\frac{T_1T_2}{T_2-T_1}\right)\right] \qquad (4)$$

From Table 3, it is evident that in all cases, the (Q_{ads}) values are negative and ranging from -3.62 to -105.53 kJ.mol^{-1}. The negative values show that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature.[19]

Table 3: Energy of activation (Ea), heat of adsorption (Qads) and free energy of adsorption (ΔG^0a) for aluminum in 0.05M TCA contain Inhibitors.

System	I.C. mM	Mean Ea from Eq (2) kJ.mol^{-1}	Ea from Arrhenius plot kJ.mol^{-1}	Qads (kJ.mol^{-1})		Mean Value (kJ.mol^{-1})		
				313 – 323 K	323 - 333 K	ΔG^0a	ΔH^0a	ΔS^0a
Blank	-	33.83	32.61	-	-	-	31.18	-
Thiourea	5	45.68	43.26	-15.08	-94.41	-21.81	43.03	0.2061
	10	47.24	45.29	-20.64	-81.19	-20.58	44.59	0.2069
	15	52.52	50.20	-16.40	-89.30	-20.72	49.88	0.2239
	20	69.88	66.91	-42.66	-105.53	-21.40	67.24	0.2817
Isomethyl thiourea	5	37.07	35.72	-10.94	-9.60	-22.90	34.43	0.1800
	10	37.08	35.70	-6.64	-13.28	-21.21	34.44	0.1748
	15	37.85	36.40	-5.85	-17.67	-20.32	35.21	0.1745
	20	40.44	37.20	-3.62	-23.95	-19.76	37.80	0.1811

Table 4: Polarization data and inhibition efficiency of thiourea & isomethyl thiourea for aluminum in 0.01 M TCA.

Inhibitor Concentration: 5 mM, **Effective Specimen area: 0.0932 dm²**

System	Ecorr mV	Icorr A/cm²	Tafel slope (mV / decade)			Inhibition efficiency %	
			-βc	+βa	B mV	Pol. method	Wt. loss method
Blank	-755	0.0820	6250	231	97	_	_
Thiourea	-782	0.027	833.33	166.67	60.31	67.07	67.24
Isomethyl thiourea	-747	0.049	1833.33	285.71	107.33	40.24	34.89

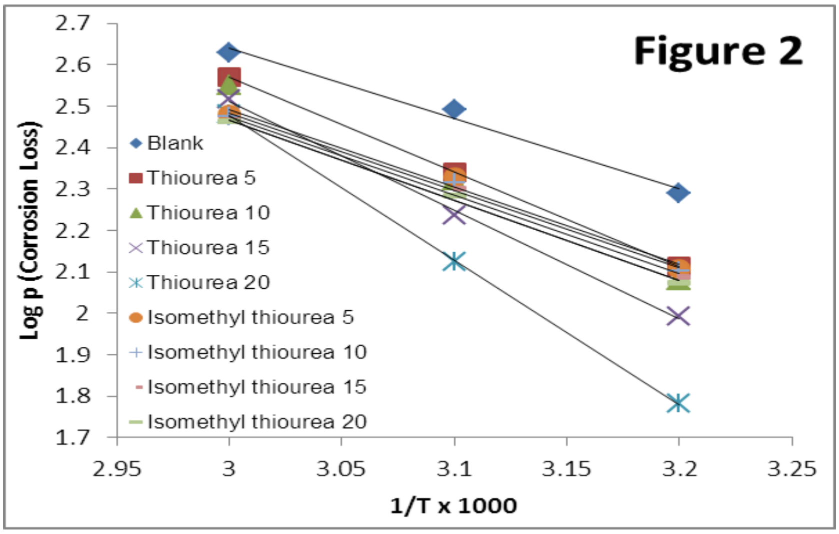


Figure 2: Arrhenius plots for corrosion of Aluminum in 0.05 M TCA in absence and presence of inhibitor.

Mean 'E_a' value was calculated by using eq. (5) for aluminum in 0.05 M TCA is 33.83 $kJ.mol^{-1}$ while in acid containing inhibitor, the mean E_a values are found to be higher than that of an uninhabited system (Table 3). Higher values of mean sea indicate physical adsorption of the inhibitors on metal surface **[20]**, which leads to an increase in the energy barrier for the corrosion process. The values of a calculated from the slope of an Arrhenius plot (Figure 2) and using eq. (5) are almost similar. Energy of activation (Ea) has been calculated from the slopes of log p versus 1/T (p = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$L\log\frac{P_2}{P_1}=\frac{Ea}{2.303R}\left[\left(\frac{1}{T_1}\right)-\left(\frac{1}{T_2}\right)\right] \qquad (5)$$

Where p_1 and p_2 are the corrosion rate at temperature T_1 and T_2 respectively. The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated using the following equation (6) and (7).

$$\Delta H^0 ads = Ea - RT \qquad (6)$$

$$\Delta S^0{}_{ads} = \frac{\Delta H^0{}_{ads} - \Delta G^0{}_{ads}}{T} \qquad (7)$$

The enthalpy changes (ΔH^0_a) are positive, indicating the endothermic nature of the reaction suggesting that higher temperature favors the corrosion process.**[21]** The entropy (ΔS^0_a) values are positive, confirming that the corrosion process is entropically favorable.**[22]**

The value of the corrosion potential with inhibitors were found become more negative than the without inhibitors. Polarization study reveals that the inhibitors function as little anodic, but significant cathodic inhibitors, the curves showed that inhibitor functions as a mixed inhibitor. The values for the Tafel parameters obtained from this plot with and without inhibitors are given in Table 4. The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency (η %) was calculated using the Equation (8). The inhibition efficiency from Tafel plots agrees well (within ± 6 %) with the values obtained from weight loss data.

$$\eta(\%) = \left[\frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)}\right] \times 100 \qquad (8)$$

Mechanism: The dissolution of aluminum in TCA the reaction in the initial stages appear to be as equation- 9.

$$3CCl_3COOH + Al \rightarrow [CCl_3COO]_3Al + 3H \qquad (9)$$

Meites and Meites [23] have demonstrated that TCA is quantitatively reduced at a mercury cathode whose potential is suitably controlled .

$$CCl_3COO^- + H^+ + 2e^- \rightarrow CHCl_2COO^- + Cl^- \qquad (10)$$

TCA gets reduced to acetic acid and hydrochloric acid by potassium amalgam or on electrolysis between electrodes of amalgamated zinc.[24]

$$CCl_3COOH + 6H \rightarrow CH_3COOH + 3HCl \qquad (11)$$

During corrosion of aluminum it is, therefore, possible that reaction (4.9) is followed by the reduction of TCA to dichloroacetic acid as a first stage.

$$CCl_3COOH + 2H \rightarrow [CHCl_2COOH + HCl \qquad (12)$$

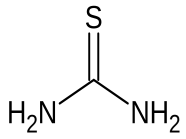
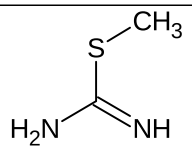
Further reduction of dichloroacetic to monochloroacetic and finally to acetic acid perhaps requires strong reducing conditions and, therefore, seems improbable.

Thus it can be generalized that the corrosion of aluminum in TCA is governed in the initial stages by the amount of the acid present while after certain period of immersion it is governed by the extent, of reduction of TCA.

The hydrochloric acid produced by the above reaction (4.9) would further react with aluminum librating hydrogen.

$$Al + 3HCl \rightarrow AlCl_3 + 3H \qquad (13)$$

The hydrogen librated would in turn further reduce tichloroacetic acid and a cycle would thus be set up. As a result of these reactions the chloride content and the acidity of the solution are likely to increase, thus resulting in increased corrosion.[25]

	
thiourea	**Isomethylthiourea**

Mann [26] has suggested that organic substances forms onium ions from the cations in acidic solutions and thus get adsorbed on the cathodic portion of the metallic surface. Most 0rganic inhibitors are compounds with at least one polar unit, having atoms of nitrogen, oxygen, sulfur and in some cases, selenium and phosphorus. According to Hackerman [27] amine type inhibitors have electron-donating ability and their action is attributed to the adsorption of the inhibitor molecules on the metal surface through an unshared pair of electrons belonging to the nitrogen atom. The same is applicable to sulphur and oxygen atoms. It seems reasonable to suppose that the presence of two polar groups ensure better attachment than single one, but this view is not universally observed. In any case, it might be asked whether two nitrogen groups would not be as sufficient as one nitrogen and one sulfur group; perhaps the answer that the two different elements serve to provide attachment at different sites, that they attach themselves to the surface probably by the nitrogen or sulfur atom, is generally accepted. According to one view, the attached molecules, extending outwards from the metallic surface like bristles of a brush, prevent the ready replenishment of acid at the metallic surface so that the acid becomes exhausted and attack becomes slow. According to another view, the molecules, attached through the polar atom or atoms, lie flat, so that each molecule covers up a considerable surface of element.

CONCLUSIONS

At all concentration of acid, as the inhibitor concentration increases inhibition efficiency increases and corrosion rate decreases. As the temperature increases corrosion rate increases in plain acid. Addition of inhibitors in corrosive media indicates that as the temperature increases corrosion rate increases while inhibition efficiency decreases. In all cases, the value of heat of adsorption (Q_{ads}) and the value of free energy of adsorption ($\Delta G^0{}_a$) is negative. The value of change of entropy ($\Delta H^0{}_a$) and entropy of adsorption ($\Delta S^0{}_a$) is positive. A mean value of 'Ea' in inhibiting acid is higher than the value of 'Ea' in plane acid.

ACKNOWLEDGEMENT

The author is thankful to Department of Chemistry, Arts, Science and Commerce College, Kholwad, Surat for providing laboratory facilities.

REFERENCE

1. Binger W W, Corrosion resistance of metal and alloy, (edited by Laque F L & Copson H R, Reinhold Publishing Corp, New York), 1963; 183.
2. Rengamani S, Muralidharan S, Kulandainathan M A & Venkatakriskna I S , J Appl Chem, 1994; 24: 355.

3. Vrsalovic L, Kliskic M, Radosevic J & Gudic S, J Appl Electrochem, 2005; 35: 1059-1065.
4. Ekpe U J, Okafor P C, Ebenso E E, Offiong O E, & Ita B I, Bull of Electrochem, 2001; 17: 131-135.
5. Kliskic M, Radosevic J, Gudic S & Katalinic V, J Appl Electrochem, 2000; 30: 823 – 830.
6. Maayta A K, & Al-Rawashdey N A F, Corr Sci, 2004; 46:1129-1140.
7. Moussa M N, Fouda A S, Taha A I & Elnenaa A, Bull. Korea Chem. Soc, 1998; 9: 192–195.
8. Al-Mayouf A M, Corr Prev Ctrl, 1996; 6 : 68-74.
9. Vashi, R. T. & Desai, P. S. Aminoacetanilides as corrosion inhibitors for aluminum in trichloroacetic acid. Bulletin of Electrochemistry, 2007; 23: 87–93.
10. Desai, P. S. & Kapopara, S. M. Inhibitive Efficiency of Inhibiting effect of anisidines on aluminum corrosion in hydrochloric acid. Indian Journal of Chemical Technology, 2009; 16(6): 485-491.
11. Desai, P. S., Desai, S. A & Vashi, R. T. Anisidines as corrosion inhibitors for aluminum in TCA. Acta Ciencia Indica, XXXIV, 2008; (2): 209-217.
12. Desai, P. S., Desai, S. A & Vashi, R. T. Nitroanilines as corrosion inhibitors for Zinc in Nitric Acid. Journal of Environmental Research and Development, 2008; 3(1): 97-104.
13. Desai, P. S. & Vashi R.T. Performance of Phenylthiourea used as Corrosion Inhibitor for aluminum in trichloroacetic acid. Journal of Indian Chemical Society, 2009; 26(5): 547-550.
14. Uhlig H H, The Corrosion Hand Book, (John Willey & Sons Inc., New York) 1948; 41.
15. Wesley, Corrosion (International Nickel Company, New York), 1956; 51.
16. ASTM, G-31-72, Standard practice for laboratory immersion corrosion testing of metals, Annual Book of Standards (ASTM, Philadelphia, PA) 1990.
17. Abdel, A. M S. & Saied, A. E. L. Inhibiting effect of some organic......Zinc in phosphoric acid solutions. Trans SAEST, 1981; 16: 197.
18. Talati J D & Darji J M, J Indian Chem Soc, LXV, 1988; (2): 94-99.
19. Bhajiwala, H. M. & Vashi, R. T. Ethanolamine, diethanolamine and triethanolamine as corrosion inhibitors for zinc in binary acid mixture [HNO3+H3PO(4)], Bull. Electroche., 2001; 17: 441.
20. Putilova I N, Barannik V P & Balezin S A, Metallic Corrosion Inhibitors (Pergamon Press, Oxford) 1960; 30-32.

21. Agrawal, D., Gupta, K. D. & Saxena, K. K. Thermodynamics and equilibrium study of the formation of binary and tertiary complexes of Co+2, Ni+2,Cu+2 and Zn+2 with (DL)-2,5 Diamino -1-pentanoic acid as secondary ligand and 2',2'-Biperidine (2',2'-Bipy) as primary ligand. Trans. SAEST, 2003; 38: 111-114.
22. Issa, R. M., El-Sonbati, A. Z., El-Bindary, A. A. & Kera, H. M. Polymer complexes XXXIV. Potentiometric and thermodynamic studies of monomeric and polymeric complexes containing 2-acrylamidosulphadiazine, Eur Polym J, 2008; 38: 561.
23. Meites & Meites. Anal. Chem., As quoted by Skoog & West in Fundamental of Analytical Chemistry. 1956; 19: 451.
24. Finar, I. L. Organic Chemistry I (The English Language Book Society and Longmas Green and Co. Ltd., London), 1962; 171.
25. Talati, J. D. & Patel, B.M. (1970). Ind. J. Tech., 1970; 8: 228-230.
26. Mann, C. A. (1936). Trans Electrochem. Soc., 1936; 69: 116.
27. Haickerman, N. & Makrides, A. C. (1954). Ind. Engg. Chem., 1954; 46: 523.