Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **3(11),** 82-89, November **(2013)** *Res. J. Chem. Sci.*

Corrosion Inhibition of Zinc by a New Inhibitor in Hydrochloric Acid Medium

Sachin H.P.[1*], Praveen B. M.[2] and Abd Hamid S.B.[3]
[1]Department of Chemistry, Jawaharlal Nehru National College of Engineering, Shivamogga-577204, Karnataka, INDIA
[2]Department of Chemistry, Srinivasa School of Engineering, Mukka, Mangalore, Karnataka, INDIA
[3]Nanotechnology and Catalysis Research Centre [NANOCAT], IPS Building, Universiti Malaya, 53100, Kuala Lumpur, MALAYSIA

Available online at: www.isca.in, www.isca.me
Received 6th November 2013, revised 13th November 2013, accepted 18th November 2013

Abstract

Electrochemical reduction of nitrobenzotriazole was carried out on lead cathode in acidic ethanol medium. The catholyte containing the reduced compound was used as corrosion inhibitor for zinc in hydrochloric acid medium. The inhibition efficiency of the catholyte was studied by weight loss and potentiodynamic polarization methods. The optimum amount of catholyte required for maximum corrosion inhibition was established. The wieght loss of zinc was decreased with increase in the concentration of inhibitor. The OCP of zinc shifted towards more cathodic direction indicating the increase of hydrogen over voltage and decrease of metal dissolution. The protection efficiency was increased with increase in inhibitor concentration and also with time indicating the progressive adsorption of reduced compounds of the catholyte. The mechanism of adsorption follows Temkins adsorption isotherm. The SEM images of zinc and corroded zinc surfaces showed the effectiveness of the catholyte in hindering the corrosion process.

Keywords: Electrochemical reduction, aminobenzotriazole, inhibitor, polarization, adsorption.

Introduction

Metals are backbone for industries and their usage is increasing due to their applications in new areas besides conventional sectors. Zinc is one such metal find extensive applications in industries; also it is widely used for the corrosion protection of steel[1-4]. In these applications, the zinc surface is exposed to various environments, which results in loss of metal and deterioration of its surface5. In order to enhance the service life of zinc material, precautions should be taken for controlling the zinc corrosion.

Many methods were discussed in the literature to control zinc corrosion. They are chromating, modification of surface using chelating agents, use of inhibitors etc[5-7]. Most of the existing methods are toxic in nature and inhibition effect also not satisfactory.

Most of these inhibitors are organic compounds containing nitrogen, sulphur, oxygen[8-12] etc. The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecule such as functional groups, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density at the donor atoms and p-orbital character of donating electrons and electronic structure of the molecule. It is reported that smaller inhibitor molecule are efficient because they facilitates electronic interactions and impede steric effects[13-15]. But many of them are toxic even though they exhibit good inhibition action.

Few organic compounds are synthesized electrochemically and the use of such compounds for corrosion inhibition studies is limited. In many electrochemical synthesis, apart from main product few intermediates are also generated and all these are present in either anolyte or catholyte portion of electrolytic cell.

The present work reports the use of catholyte containing aminobenzotriazole (ABT) as corrosion inhibitor. The aminobenzotriazole was synthesized using nitrobenzotriazole (NBT) in an electrolytic cell containing lead as cathode and platinum as anode. The electrolyte was 20% acidic ethanol. After completion of electrolysis, the entire catholyte was neutralized and the same was used in small proportion as corrosion inhibitor.

Material and Methods

Experimental Part: All the chemicals used in this work were of AR grade (S. D. fine chemicals, Mumbai, India). The test solutions were prepared with doubly distilled water. The nitration of benzotriazole was carried out with the procedure given elsewhere[16]. The NBT was subjected to electrochemical reduction in a H shaped cell to get aminobenzotriazole (ABT). The electrolyte was 10% alcoholic sulphuric acid containing 1% NBT. The capacity of electrolytic cell was 150ml with lead electrode in cathode compartment and platinum in anode comportment. The anolyte and catholyte were separated by a porous frit, which was in between the two compartments. The saturated calomel electrode (SCE) was employed as reference electrode and placed in the cell such that the tip of the bend

portion was very close to the cathode surface. The working electrode was lead plate of 99.99% pure.

The macroscale electrolysis was performed at 303K under galvanostatic condition using Galvanostat PS-618, Chemilink system, Mumbai, India. The electrolysis was carried out at 0.8V v/s SCE and a current of 500mA. The progress of the electrolysis was tested by TLC. The electrolysis was stopped when all the starting material converted into product. The completion of the reaction was established qualitatively by dye test which generally applied for the confirmation of ammine group. The resulting catholyte was neutralized to pH 7 using sodium bicarbonate solution and the neutralized catholyte was used for the corrosion inhibition studies.

The commercial Zinc sheet [composition Cu=0.17%, Ti=0.075%, Al<0.05%, Pb-Cd<0.03%, Fe=0.02%, Sn=0.001%, Mg=0.0005%) and remainder being Zn] was used for the corrosion studies. For weight loss measurement, the coupons measuring 1 x 2 x 0.2 cm^3 were polished with emery papers of different grit size (600-1200), washed with deionized water, degreased with absolute alcohol, dried, and then etched in 2 M HNO_3 solution for 10 s. The etched electrode was rinsed with deionized water immediately followed by rinsing with absolute ethanol. The weight loss (in mg cm^{-2}) was determined at different immersion time at 298 K by weighing the cleaned samples before and after immersing the coupons into 100 cm^3 of corrosive solution in the absence and presence of various concentration of catholyte.

For polarization study, 1cm^2 area of zinc coupons was exposed and the remaining portion was covered with araldite. The coupons were cleaned in the similar manner as explained above. The experiments were performed in a three electrode cell at 298K using platinum and SCE as auxiliary and reference electrode respectively. The SCE was connected via luggin capillary, the tip of which is very close to the electrode surface. The measurements were carried out in aerated, non stirred solution with and without catholyte. The anodic and cathodic polarization curves for the treated and untreated zinc specimens were obtained under galvanostatic conditions.

The surface morphology of zinc specimens before and after polarization study in the presence of inhibitor was tested by SEM.

Results and Discussion

Weight loss measurements: Figure 1 shows the variation of the weight loss (in mg cm^{-2}) of zinc with the immersion time in 0.2 M HCl solution in the presence of various concentrations (0.2 to 1.0%) of catholyte at 298K. It is evident from figure 1 that the weight loss decreased with increase in the concentration of catholyte in corrosive medium. The minimum weight loss was observed in the solution containing 0.6% of catholyte and above 0.6% there was no change in the weight loss.

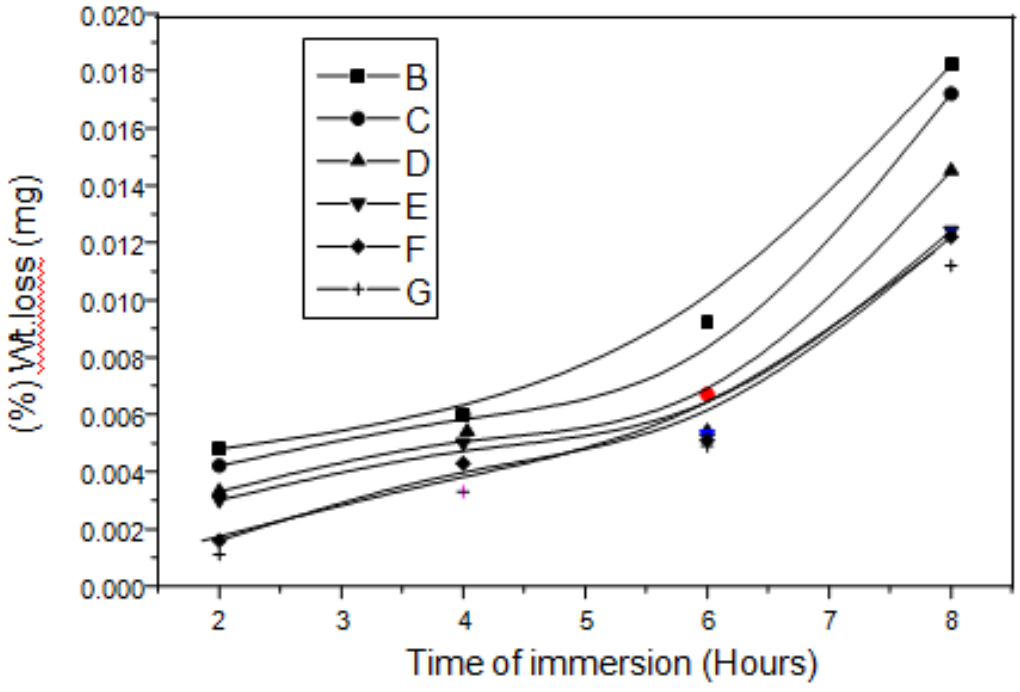

Figure-1
Variation of weight loss with time of immersion in 0.2M HCl at different concentration of inhibitor (B=blank, C=0.2%, D=0.4%, E=0.6%, F=0.8%, G=1.0%)

The decrease in weight loss in the presence of catholyte suggested that the ABT present in the corrosive medium get adsorbed on zinc surface and the extent of surface coverage increases with increase in the amount of inhibitor up to 0.6%. The curves in figure 1 also indicated that there was gradual decrease in weight loss of zinc metal with increase in inhibitor concentration. All the curves were similar and exhibiting two kinds of metal loss indicating different rate of dissolution. The rate of weight loss was increased with increase in the time of immersion.

Figure 2 shows the variation of weight loss with inhibitor concentration (0.1-1.0%) at different acid strengths for immersion time of 2 hours at 303K. The curve (1) in the figure 2 indicated that the weight loss is minimum for all inhibitor concentration in 0.2 M acid solution. Further for a given acid strength the weight loss decreased with increase in inhibitor concentration. The weight loss of zinc attains a stable value after 0.6% of inhibitor concentration. The curve (2) is for 0.4 M acid solution and here also the same trend was observed and the curve (3) is for 0.6M acid strength.

The inhibition efficiency (%IE) (table 1) was calculated from the total weight loss by the equation.

$$IE\ (\%) = \left[1 - \frac{WL}{WL^0}\right] X\ 100$$

Where: WL^0 and WL are the weight losses of specimens without and with inhibitor.

Polarization measurements: Effect of inhibitor concentration: The cathodic and anodic polarization curves of zinc in the presence and absence of inhibitor with different acid concentration are shown in figure 3, 4 and 5. In the presence of inhibitor, the cathodic and anodic curves are shifted and the shift is depends on inhibitor concentration. The polarization curve for the untreated zinc sample shows that in the anodic region the current density increases rapidly indicating extensive dissolution of metal.

The polarization parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}) obtained by extrapolation of the Tafel lines are listed in table 2, 3 and 4. As the concentration of inhibitor increases, there is a marginal shift in E_{corr} and a decrease in I_{corr}. The addition of inhibitor hinders acid attack on zinc and a comparison of curves in both the cases shows that with increase in the inhibitor concentration there is a consistent decrease in anodic and cathodic current densities, indicating that the prepared compound acts as mixed type inhibitor.

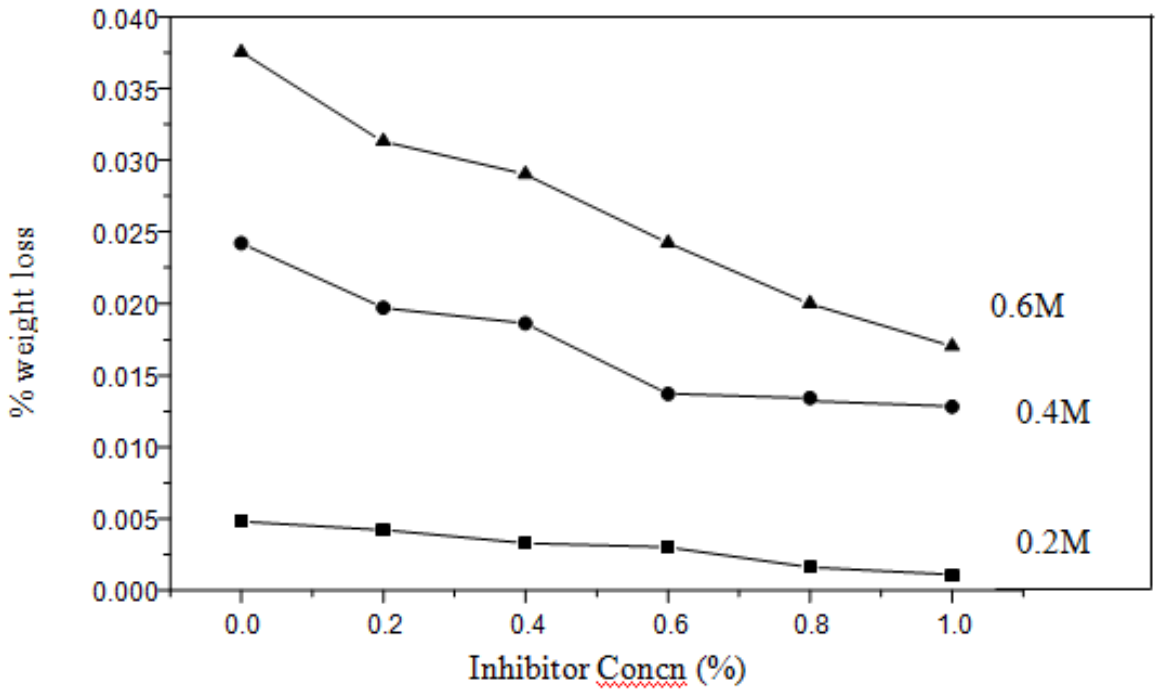

Figure-2
Variation of weight loss with inhibitor concentration for different acid concentration (Immersion time 2 Hrs)

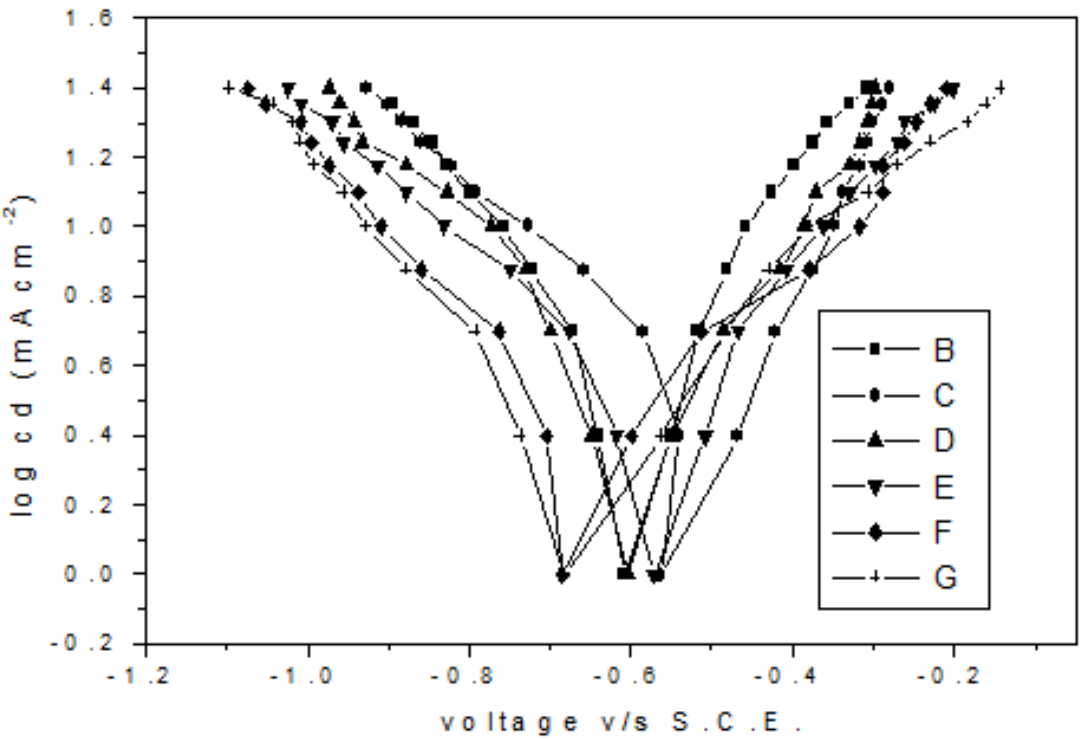

Figure-3
Anodic and cathodic polarization curves of zinc in 0.2M HCl (B=blank, C=0.2%, =0.4%,E=0.6%,F=0.6%,G=0.8%)

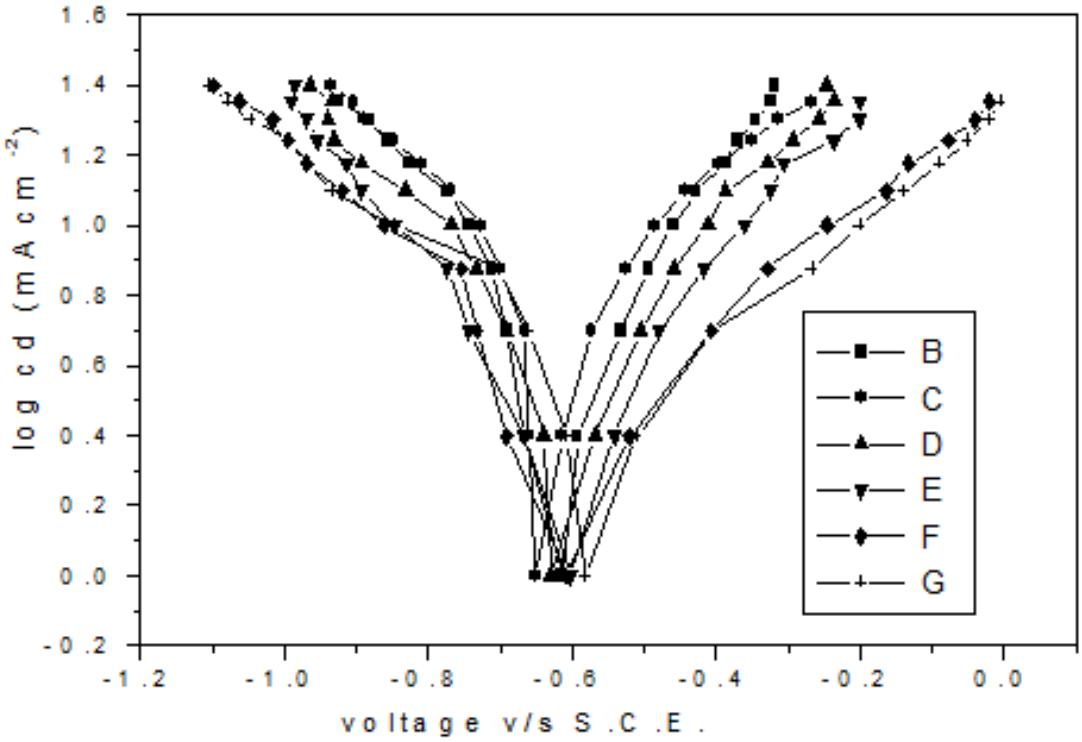

Figure-4
Anodic and cathodic polarization curves of zinc in 0.4M HCl (B=blank, C=0.2%, D=0.4%,E=0.6%,F=0.6%,G=0.8%)

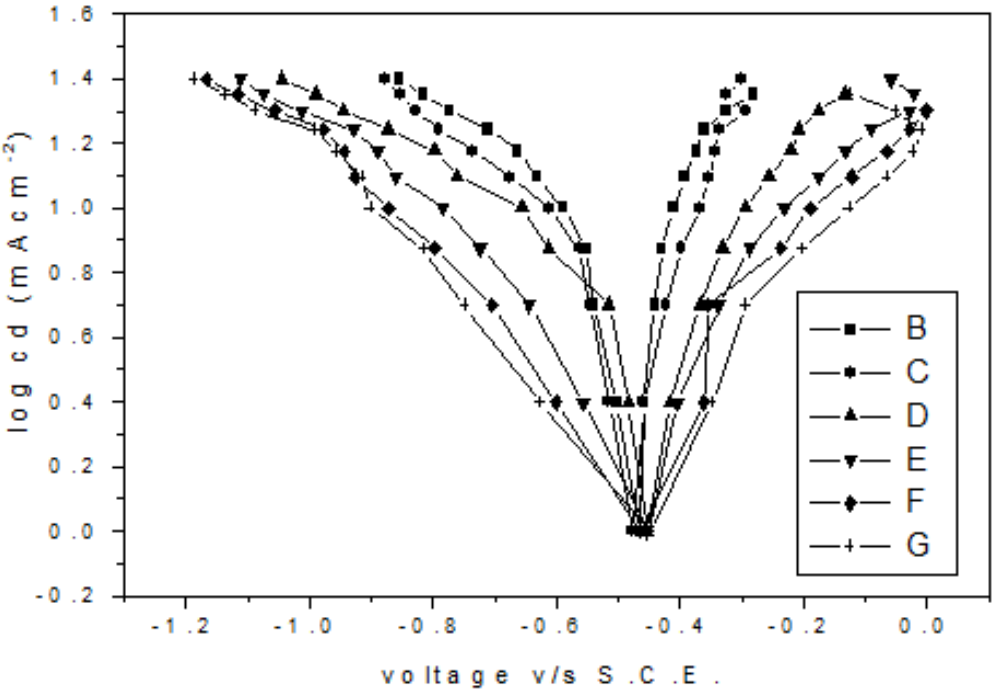

Figure-5
Anodic and cathodic polarization curves of zinc in 0.6M HCl (B=blank, C=0.2%, D=0.4%,E=0.6%,F=0.6%,G=0.8%)

Table-1
The variation of %IE with immersion period by weight loss method

Concentration of inhibitor (%)	Immersion time	% Inhibition Efficiency (Acid Concentration)		
		0.2M	0.4M	0.6M
0.2	2Hrs	12	18	06
0.4		31	23	26
0.6		35	43	29
0.8		56	44	34
1.0		76	47	40
0.2	4Hrs	--	14	05
0.4		10	21	19
0.6		16	31	19
0.8		28	38	29
1.0		45	46	33
0.2	6Hrs	27	15	16
0.4		41	23	22
0.6		42	28	35
0.8		44	47	46
1.0		46	47	44
0.2	8Hrs	05	14	05
0.4		20	15	50
0.6		31	25	52
0.8		32	32	55
1.0		38	37	55

Table-2
Electrochemical parameters and inhibition efficiency for corrosion of Zinc in 0.2M HCl

Concentration of Inhibitor(mL)	E_{corr} (V)	$-b_c$ (vcm^{-1})	b_a (vcm^{-1})	I_{corr} ($mAcm^{-2}$)	η (%)
Blank	-0.56	0.50	0.31	5.75	
0.2	-0.54	0.56	0.33	5.01	12
0.4	-0.52	0.40	0.30	4.26	25
0.6	-0.53	0.66	0.34	3.89	32
0.8	-0.50	0.52	0.31	2.18	62
1.0	-0.48	0.53	0.30	2.04	64

Table-3
Electrochemical parameters and inhibition efficiency for corrosion of Zinc in 0.4M HCl

Concentration of Inhibitor(mL)	E_{corr} (V)	$-b_c$ (vcm^{-1})	b_a (vcm^{-1})	I_{corr} ($mAcm^{-2}$)	η (%)
Blank	-0.56	0.70	0.56	7.76	
0.2	-0.63	0.55	0.55	7.24	06
0.4	-0.60	0.45	0.55	5.01	35
0.6	-0.57	0.45	0.55	4.70	38
0.8	-0.59	0.55	0.53	3.80	51
1.0	-0.52	0.59	0.58	3.54	59

Table- 4
Electrochemical parameters and inhibition efficiency for corrosion of Zinc in 0.6M HCl

Concentration of Inhibitor(mL)	E_{corr} (V)	$-b_c$ (vcm^{-1})	b_a (vcm^{-1})	I_{corr} ($mAcm^{-2}$)	η (%)
Blank	-0.46	0.60	0.43	9.12	
0.2	-0.44	0.45	0.47	7.76	14
0.4	-0.40	0.64	0.45	5.24	42
0.6	-0.40	0.35	0.46	4.78	47
0.8	-0.43	0.60	0.42	3.60	60
1.0	-0.43	0.61	0.50	3.40	68

The change in the values of cathodic Tafel slope b_c with change in inhibitor concentration clearly indicates that the prepared compound influence the kinetics of hydrogen evolution reaction. However, the values of anodic Tafel slope b_a, increases only to a small extent, as these compound do not influence anodic dissolution. This indicates an increase in the energy barrier for proton discharge leading to less gas evolution. The value of IE increased with increase in inhibitor concentration, which indicates higher surface coverage in a solution with maximum concentration of inhibitor.

By comparing polarization curves in the absence and presence of inhibitor it was observed that increase in inhibitor concentration shifts the corrosion potential (E_{corr}) in the positive direction and reduced both anodic and cathodic current densities. These results revealed that the presence of aminobenzotriazole inhibits both anodic and cathodic processes. The action of inhibitor may be related to adsorption and formation of a passive film on the zinc surface, which was confirmed by SEM examination of the electrode surface.

The protection efficiency (η) was calculated using the following expression

Where: I^0_{corr} and I_{corr} are the corrosion current densities before and after treatment.

$$\eta = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100$$

Effect of acid concentration: The influence of acid concentration on the dissolution of zinc was studied. The protection efficiency of the inhibitor was found to be constant up to a concentration of 0.6M HCl. When the concentration of acid increased beyond 0.6M the protection efficiency was decreased. At higher acid concentration the hydrogen evolution dominates which results in the stripping of the adsorbed compound from the metal surface and exposes the bare metal to corrosive environment.

Adsorption Isotherm: Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. Inhibition efficiency increases with increase in inhibitor concentration; this confirms the progressive formation of a protective layer on the metal surface and inhibits the corrosion. Plot of θ v/s log C gives a straight line and the adsorption of inhibitor on the metal surface follows the Temkin adsorption isotherm. The adsorption isotherm is shown in figure 6 The degree of surface coverage θ_{inh} was obtained using the equation

$$\theta_{inh} = \left(1 - \frac{I\,inh}{I\,uninh}\right)$$

Scanning Electron Microscopic Studies: The formation of a protective surface film of catholyte on the zinc surface was confirmed by SEM studies. SEM photomicrographs of the modified metal surface before and after anodic polarization were taken. SEM photomicrograph of the zinc specimen in the presence of catholyte before polarization study is shown in figure 7a, which shows the uniform modification of metal surface. The SEM image of the zinc sample obtained after anodic polarization study in the presence of catholyte shows some intergranular attack and rest of the surface still keeps a similar surface morphology (figure 7b) leading to the suggesion that the catholyte provides a good corrosion protection to the zinc substrate by adsorbing on the surface and covering greater surface area. This indicated that the presence of an organometallic layer on the metal surface, which inturn protect the metal loss by dissolution or hydrogen evolution in acid medium.

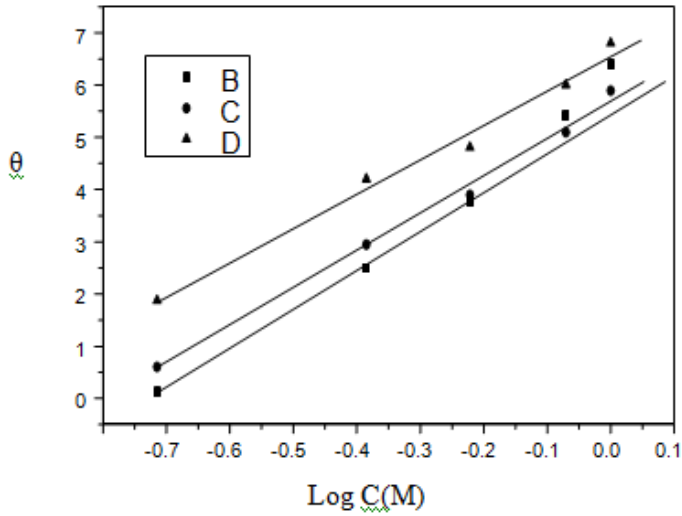

Figure-6
Temkins adsorption isotherm curves different concentration of HCl B=0.2M, C=0.4M, D=0.6M

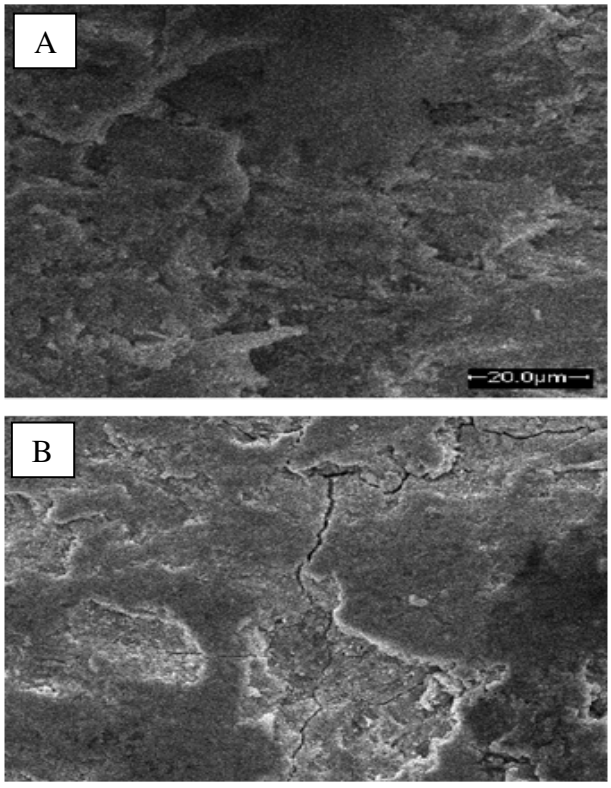

Figure-7
SEM photomicrographs of Zinc specimens A= with inhibitor before polarization, B=with inhibitor after polarization

Conclusion

Aminobenzotriazole was electrochemically synthesized. Weight loss, polarization and SEM techniques were used to study the corrosion inhibition of zinc in aerated unstirred hydrochloric acid solution at the corrosion potential using catholyte containing aminobenzotriazole. The corrosion of zinc in HCl solution is significantly reduced upon the addition of catholyte. The inhibition is due to the adsorption of ABT on the zinc surface and the blocking of active sites. Inhibition efficiency increases with increase in concentration and immersion time. SEM observation of the electrode surface showed the formation of a surface film of inhibitor on the electrode surface. This film retarded the reduction of dissolved oxygen and inhibited the growth of zinc oxide in the HCl solution (mixed type). Physisorption is proposed as the mechanism for corrosion inhibition. The mechanism of adsorption follows Tempkin adsorption isotherm.

References

1. Hinton B.R.W. and Wilson L., The corrosion inhibition of zinc with cerous chloride, *Corrosion Science,* vol. **29(8),** 967–975 **(1989)**

2. Rajappa S.K., Venkatesha T.V. and Praveen B.M., Chemical treatment of zinc surface and its corrosion inhibition studies, *Bulletin of Material Science*, **31(1),** 37–41 **(2008)**

3. Abdel-All M.S., Ahmed Z.A. and Hassan M.S., Inhibiting and accelerating effects of some quinolines on the corrosion of zinc and some binary zinc alloys in HCl solution, *Journal of Applied Electrochemistry*, **22(11),** 1104–1109 **(1992)**

4. Vashi R.T. and Champaneri V. A., Nitro anilines as corrosion inhibitors for zinc in sulfamic acid, *Bulletin of Electrochemistry*, **13(8-9),** 353–357 **(1997)**

5. Du T., Chen J. and Cao D., N, N-Dipropynoxy methyl amine trimethyl phosphonate as corrosion inhibitor for iron in sulfuric acid, *Journal of Materials Science*, **(36),** 3903–3907 **(2001)**

6. Stupnisek-Lisac E., Podbrscek S. and. Soric T., "Non-toxic organic zinc corrosion inhibitors in hydrochloric acid," *Journal of Applied Electrochemistry*, (**24),** 779–784 **(1994)**

7. Wippermann K., Schaltze J.W., Kessel R., and Penninger T. The inhibition of zinc corrosion bybisaminotriazole and other triazole derivatives, *Corrosion Science*, (**32),** 205–223 **(1991)**

8. James A.O. and Akaranta O., Inhibition of Zinc in Hydrochloric acid solution by Red Onion Skin Acetone extract, *Res. J. Chem. Sci.,* **1(1),** 31-37 **(2011)**

9. Vasudha V.G. and Shanmuga Priya K., Polyalthia Longifolia as a Corrosion Inhibitor for Mild Steel in HCl Solution, *Res. J. Chem. Sci.,* **3(1),**21-26**(2013)**

10. Bhajiwala H.M. and Vashi R.T., Ethanolamine, diethanolamine and triethanolamine as corrosion inhibitors for zinc in binary acid mixture [HNO_3+H_3PO_4], *Bulletin of Electrochemistry*, **17(10),** 441–448 **(2001)**

11. Muller B. and Forster I., Inhibition of zinc pigments in aqueous alkaline media by aromatic hydroxy compounds, *Corrosion Science*, **52(10),** 786–789 **(1996)**

12. Fiaud C., Bensarsa S., Des Aulnois I. D., et al., Inhibiting properties of phosphines against zinc corrosion in acidic media, *British Corrosion Journal*, (**22),**109–114 **(1987)**

13. Prabhu R.A., Venkatesha T.V. and Praveen B.M., Electrochemical Study of the Corrosion Behavior of Zinc Surface Treated with a New Organic Chelating Inhibitor, *ISRN Metallurgy* Volume 2012, Article ID 940107, 6 pages doi:10.5402/2012/940107

14. Ihara M., Nishihara H. and Aramaki K., Mechanism of corrosion inhibition with bismuth compounds for iron, nickel and zinc in acid solutions, *Denki Kagaku*, (**60),**500– 507 **(1992)**

15. Muller B. and Imblo G., Heterocycles as corrosion inhibitors for zinc pigments in aqueous alkaline media, *Corrosion Science*, (**38),** 293–300 **(1996)**

16. Morris R.T. and Boyd R. N, *Organic Chemistry*, Pretice-Hall of India Pvt, (**1973)**