THE INHIBITION EFFECT OF THIAZINE COMPOUNDS TOWARDS THE CORROSION OF MILD STEEL IN SULPHURIC ACID MEDIA

V.Hemapriya*, K.Parameswari and G.Bharathy

Department of Chemistry, PSGR Krishnammal College for Women,
Coimbatore-4, Tamilnadu, India.
*E-mail:hemahimaa@yahoo.co.in

ABSTRACT

The inhibition effect of thiazines (AT, CBT & NBT) on mild steel corrosion in 1M sulphuric acid (H_2SO_4) was investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The result showed that corrosion rate was significantly decreased in presence of the inhibitors. The inhibiting action increases with the concentration of thiazine compounds to attain 99 % at 0.5mM of (AT). The increase in temperature leads to a decrease in the inhibition efficiency of the compounds in the temperature range 308-353K. Adsorption of thiazines on the mild steel surface in 1M H_2SO_4 obeyed the Langmuir adsorption isotherm. EIS measurements showed an increase in charge transfer resistance (R_{ct}) with concentration. Potentiodynamic polarization study showed that the inhibitors act as mixed type, controlling both the anodic and cathodic reactions. Surface analysis by SEM confirmed the formation of adsorbed protective layer of the inhibitor on the steel surface.
Keywords: Thiazines, mild steel, Corrosion, inhibition efficiency, EIS, SEM.

INTRODUCTION

Heterocyclic compounds represent a potential class of corrosion inhibitors. Corrosion inhibition by N-containing heterocyclic compounds has been widely reported. Heterocyclic compounds containing both N&S atoms are of particular importance as they often provide excellent inhibition compared to those containing only N or S. The planar Π electrons and lone pair of electrons present on the heteroatoms are the important structural features that determine the adsorption of these molecules on the metal surface.

Although a vast number of heterocyclic compounds have been reported as corrosion inhibitors, no work has so far been reported on the use of 1,3 – thiazines as corrosion inhibitors for the metals especially mild steel.

Thiazine is a 6 membered ring system which contains two heteroatoms (N&S) placed at 1, 3 – positions. Thiazines are very useful units in the field of medicinal chemistry and have been reported to exhibit a variety of biological activities. The 2- substituted imino group of the thiazine ring exhibits promising biological activities. Chalcones are very versatile substrates for the synthesis of thiazines by reaction with thiourea.

The aim of this work is to synthesize 2- amino 1,3 thiazine derivatives and to evaluate their anticorrosion potential on mild steel in acid media.

EXPERIMENTAL

Mild steel strips of composition C=0.079%, P=0.025%, Mn=0.018%,S=0.021% and the remainder iron were used for weight loss method.

Synthesis of inhibitors

The thiazines are synthesized by cyclising the chalcones with thiourea and have the structures[1] (Fig.-1).

FTIR spectral data of 1,3-thiazine

IR peaks at position 1655 cm^{-1} are due to N-H stretching mode of amino group. The peak at 2362cm^{-1} and 1602 cm^{-1} corresponds to C-S-C stretching and C=N stretching of thiazine ring respectively. Peak at 1495cm^{-1} is assigned to aromatic C=C stretching.

Corrosion monitoring methods
Weight loss method

Mild steel specimens of size 3 cm X 1 cm X ☐0.05 cm were pickled with concentrated HCl. The plates were washed, dried and polished successively using emery sheets of 1/0, 2/0, 3/0 and 4/0 grades to remove adhering impurities degreased with trichloroethylene and dried. The plates were kept in a desiccator to avoid the absorption of moisture. The initial weights of the polished plates were taken. A blank solution of 1M H_2SO_4 and various concentration solutions of the inhibitors were taken in a 100ml beaker and the steel specimens were suspended in the solution using glass hooks. Care was taken to ensure that the specimens were immersed completely in the solution and the specimen does not touch the walls of the beaker. After a period of three hours, the specimen were taken out, washed with running water, dried and weighed. From the initial and final weight of the specimen weight loss was calculated. Inhibition efficiency was calculated from the weight loss of the specimen. To know the effect of temperature, the weight loss experiment was carried out at various temperatures (303 K – 333 K).
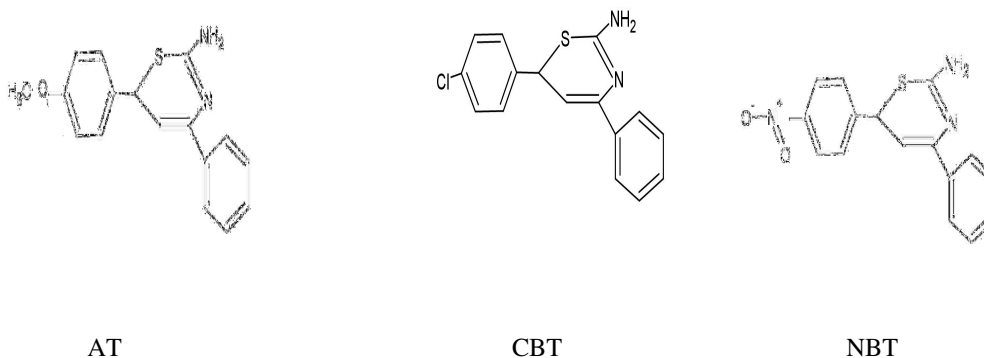

AT   CBT   NBT

Fig.-1 Structure of the inhibitors

Electro chemical studies

Electrochemical impedance and polarization measurements were carried out using Compact stat Electrochemical system (Ivium, Netherlands). The frequency range for EIS measurements was 1MHz to 10MHz with applied potential signal amplitude of 10 mV around the rest potential. The measurements were carried out in a three electrode cell assembly. Platinum and saturated calomel electrodes were used as counter and reference electrodes respectively. The same mild steel specimen in the form of cylindrical rod, embedded in Teflon, with an exposed area of $0.785cm^2$ was used as working electrode.

The exposed area was mechanically abraded with a series of emery papers of variable grades, washed with distilled water, degreased with trichloro ethylene and finally washed with water. Before measurements the working electrode was immersed and left for 10 min at the open circuit potential. Polarization measurements were obtained at a scan rate of 10 mV/ min. All measurements were made at 30 ± 1^oC in solutions open to the atmosphere under unstirred conditions.

Synergistic effect of halide ions

The synergistic effect was studied in the presence of 1mM KCl, KBr and KI to the steel specimen immersed for 3 hours in 1M H_2SO_4 containing various concentration of the inhibitor. The weight loss method procedure was followed to study the synergistic effect.

RESULTS AND DISCUSSION
Weight Loss Method

The inhibition efficiency with different concentration of the inhibitors (AT, CBT&NBT) on the mild steel in 1M H_2SO_4 has been evaluated by weight loss measurements and the results are summarized in Table-1. The data revels that inhibition efficiency increases with increase in concentration of the inhibitors. The

behavior may be attributed to an increase in surface coverage (θ) by the adsorption of inhibitor on the mild steel surface, in the aggressive solution, which restricts the dissolution of the metal.

Effect of temperature

The effect of temperature on the inhibited acid-metal reaction is highly complex because many changes occur on the metal surface such as rapid etchings, desorption of the inhibitor and the inhibitor may undergo decomposition and/ or rearrangement. To evaluate the effect of temperature on the adsorption behavior as well as to determine the activation parameters of the corrosion of mild steel in 1M H_2SO_4 solution and 1M H_2SO_4 solution containing the inhibitors, the weight loss measurements were carried out in the temperature range of 303-333K and the results are presented in Table-2. The data revel that as the temperature is increased the corrosion rate increased and the inhibition efficiency decreased. The decrease in the inhibition efficiency with increase in temperature may be attributed to the increase in the solubility of the protective film or the reaction products precipitated on the surface of the metal that might otherwise inhibit the reaction [2-3]. This is in accordance with Ergun et al [4].

The corrosion rate (CR) of the mild steel in acidic media is related to the temperature by the Arrhenius equation-

$$\text{Log CR} = \log A - Ea/\ 2.303\ RT$$

Where CR is the corrosion rate, Ea is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. The plot of log CR vs 1/T is shown in Fig.-2.

Linear plots were obtained. The values of Ea were calculated from the slope of the straight lines and are given in Table-3. The relationship between the temperature dependence of percent inhibition efficiency (%IE) of an inhibitor and the activation energy found in its presence is given as follows [5-6] :

 (i.) Inhibitors whose inhibition efficiency decreases with temperature increase, the value of activation energy (Ea) is greater than that in the uninhibited solution.
 (ii.) Inhibitors whose % IE does not change with temperature variation, the activation energy does not change with the presence of inhibitors.
 (iii.) Inhibitors whose % IE increases with temperature increase, the value of activation energy (Ea) found is less than that in the inhibited solution.

It is clear from the Table-3 that Ea values in the presence of inhibitors are higher than that in the absence. The higher Ea values imply a slow reaction and that the reaction is very sensitive to temperature. The increase in the activation energy in the presence of inhibitors signifies physical adsorption [7]. The Gibbs free energy of adsorption (ΔG°) calculated from surface coverage θ is listed in Table-3. The negative values of ΔG° ensure spontaneity of adsorption process and the stability of the adsorbed layer on the surface of the mild steel .This stability of the adsorbed layer decreases with increase in temperature. It is clearly seen from the decrease in the absolute value of ΔG°_{ads} with the raising temperature. This also refers to physical adsorption.

Generally the values of ΔG° less negative then -40KJ mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal surface (physisorption), those more negative than -40KJ mol^{-1} involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond(chemisorptions) [8-9]. Based on the data presented in Table-3 the value of the ΔG° was found to be less negative then -40KJ mol^{-1}. This confirms the occurrence of physical adsorption.

Adsorption isotherm

Adsorption of the inhibitor molecules mainly depends on the charge and nature of the metal surface, electronic characteristics of the metal surface, temperature, adsorption of the solvent, ionic species and the electrochemical potential at the solution interface. The adsorption isotherm describes the adsorption behavior of organic compounds. The most frequently used adsorption isotherms are Langmuir, Tempkin, Frumkin and Freundlich. To obtain the adsorption isotherm, the degree of surface coverage (Θ) was calculated for various concentrations of thiazines from the weight loss data and listed in Table-1.

Adsorption behavior of thiazines is best explained by Langmuir adsorption isotherm. Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and adsorbent [10]. Assumption of Langmuir relates the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (Θ) according to the equation-

$$C/Θ = 1/K + C$$

Where 'K' is the equilibrium constant of adsorption.

A liner plot behavior has been obtained when the graph is plotted between C/Θ and C (Fig.-3).

Applicability of Langmuir adsorption isotherm to the adsorption of thiazines on mild steel confirms the formation of multimolecular layer of adsorption where there is no interaction between the adsorbate and the adsorbent [3].

Table-1: Inhibition efficiency at various concentrations of thiazine for the corrosion of mild steel in IM H$_2$SO$_4$ obtained by weight loss measurements at 30 ± 1°C

Name of the inhibitor	Inhibitor concentration (mM)	Weight loss(gms)	Inhibitor Efficiency (%)	corrosion rate (mpy)	Degree of coverage(θ)
	Blank	0.3009		7506.37	
AT	0.1	0.0154	94.88	384.17	0.9488
	0.2	0.0073	97.57	182.10	0.9757
	0.3	0.004	98.67	99.78	0.9867
	0.4	0.003	99.0	74.83	0.999
	0.5	0.001	99.16	24.94	0.9996
CBT	0.1	0.0221	92.65	551.31	0.9265
	0.2	0.0205	93.18	511.40	0.9318
	0.3	0.0199	93.38	496.43	0.9338
	0.4	0.0133	95.57	331.78	0.9557
	0.5	0.0115	96.17	286.88	0.9617
NBT	0.1	0.1063	64.67	2651.80	0.6467
	0.2	0.0805	73.24	2008.18	0.7324
	0.3	0.0638	78.79	1591.58	0.7879
	0.4	0.0435	85.54	1085.16	0.8554
	0.5	0.0244	91.89	608.692	0.9189

Table-2: Effect of temperature on inhibition efficiency of thiazines at 0.5mM concentration in IM H$_2$SO$_4$

Name of the inhibitor	Temperature(K)	Weight Loss (gms)	Inhibition efficiency (%)	Corrosion Rate (mpy)
AT	303	0.001	99.16	74.83
	313	0.0074	97.78	553.80
	323	0.0173	95.07	1294.71
	333	0.0408	88.47	3053.43
CBT	303	0.0072	96.17	538.84
	313	0.0179	94.65	1339.61
	323	0.0291	91.7	2177.81
	333	0.0424	88.02	3173.17
NBT	303	0.0164	90.24	1227.35
	313	0.0388	88.41	2903.75
	323	0.0638	81.82	4774.72
	333	0.0984	72.2	7364.15

Table-3 : Activation energy and free energy of adsorption for the corrosion of mild steel in IM H_2SO_4 at 0.5mM concentration of inhibitors

Name of the inhibitor	Ea (Kj)	ΔG^0_{ads} at various temperatures (Kj)			
		303K	313K	323K	333K
Blank	21.34	-	-	-	-
AT	101.02	-31.57	-22.10	-20.59	-18.68
CBT	48.96	-19.98	-19.73	-19.10	-18.56
NBT	49.47	-17.47	-17.54	-16.68	-15.68

Table-4: Potentiodynamic polarization parameters for thiazines at selected concentrations in IM H_2SO_4

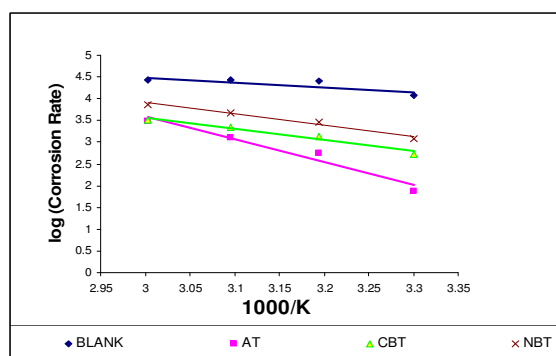| Name of the inhibitor	Inhibitor concentration mM	Tafel Slopes (mV/decade)		Ecorr (mV)	Icorr (µA/Cm2)	Inhibition efficiency (%)
		ba	bc			
AT	Blank	69	141	-474.3	3108	
	0.1	34	134	-477.7	591	80.98
	0.3	36	148	-439.1	196	93.69
	0.5	35	129	-450.2	184	94.07
CBT	0.1	28	116	-472.5	489	84.26
	0.3	35	102	-463	174	94.40
	0.5	37	89	-466.7	124	96.01
NBT	0.1	32	130	-487.8	794	74.45
	0.3	49	141	-501.3	673	78.34
	0.5	32	129	-496.5	667	78.53

Fig-2: Arrhenius plot of corrosion rate of mild steel in IM H_2SO_4 in presence and absence of the inhibitors

Polarization studies

Potentiodynamic polarisation studies on the mild steel have been made for the inhibitors in 1M H_2SO_4. Typical polarization curves are depicted in Fig 4. Corrosion kinetic parameters E_{corr}, I_{corr}, Tafel constants (ba, bc) and inhibition efficiency are presented in Table 4. The lower current density (I_{corr}) values in the presence of inhibitors without causing significant changes in corrosion potential (E_{corr}) suggest that the compounds are mixed type inhibitors and are adsorbed on the surface there by blocking the corrosion

reaction. The Tafel constant b_a and b_c are both affected and there is no definite trend in the shift of E_{corr} values. This suggests that the compounds are mixed type inhibitors.
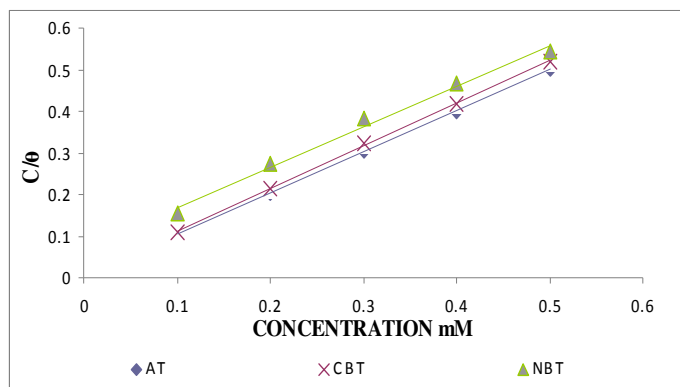

Fig-3: Langmuir's plot of the inhibitors in IM H_2SO_4

Table-5: AC impedance parameters for thiazines at selected concentrations in 1M H_2SO_4

Name of the inhibitor	Inhibitor concentration mM	Rt (ohm/cm2)	Inhibition efficiency (%)	Cdl (µA/Cm2)
AT	Blank	4.78		23.3
	0.1	35.3	86.45	14.1
	0.3	74.88	93.61	11.9
	0.5	85.46	94.40	11.3
CBT	0.1	15.08	68.30	16.2
	0.3	18.82	74.60	9.74
	0.5	73.7	93.51	7.77
NBT	0.1	8.5	43.76	20.4
	0.3	18.19	73.72	18.1
	0.5	38.38	87.54	13.6

Table-6: Synergistic effect of 1Mm KCl/KBr/KI on the inhibition efficiency of inhibitors in 1M H_2SO_4 by weight loss method at 30 ± 1° C

Name of the Inhibitar	Inhibitor concentration mM	Inhibition effeciency(%)			
		without KCl/KBr/KI	With 1mM KCl	With 1mM KBr	With 1mM KI
AT	0.02	62.35	70.28	78.62	88.16
	0.04	85.86	87.83	87.17	89.74
	0.06	89.84	90.23	93.50	94.65
	0.08	91.32	94.20	95.24	97.82
	0.10	94.88	95.64	96.18	98.14
CBT	0.02	65.62	72.37	78.43	80.14

	0.04	79.14	81.54	84.65	88.76
	0.06	84.27	86.43	89.92	90.24
	0.08	90.23	92.44	92.86	93.15
	0.10	92.65	94.08	95.18	96.74
	0.02	37.45	46.53	51.88	58.72
	0.04	44.62	59.01	57.81	60.58
NBT	0.06	46.53	60.28	62.16	65.72
	0.08	59.01	61.79	64.93	77.27
	0.10	64.67	65.08	66.18	86.86

Electrochemical Impedance spectroscopy

Typical Nyquist plots obtained in the absence and presence of different concentrations of the inhibitors are shown in Fig 5. They are semicircle and this may be attributed to the charge transfer reaction. The impedance parameters derived from Nyquist plots are presented in Table 5. From the table it is evident that as the concentration of the inhibitor increases, C_{dl} values decrease and R_t values increase. Decrease of C_{dl} is due to an increase in the thickness of the electrical double layer. This suggests that the inhibitor molecules function by adsorption at the metal solution interface.
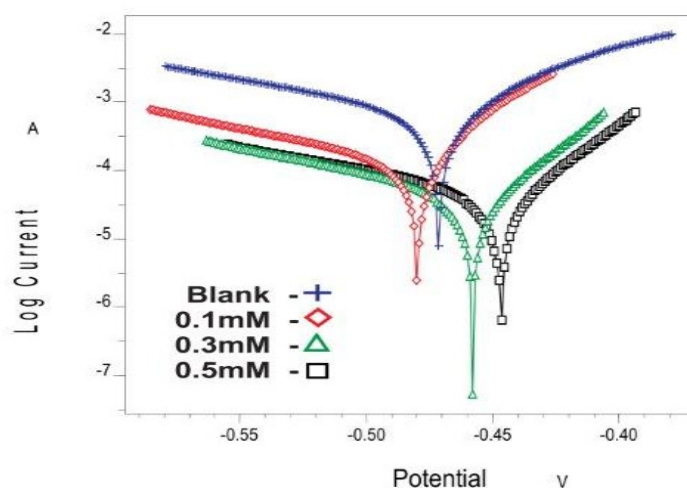
Fig-4: Polarization curve for mild steel in IM H_2SO_4 in presence and absence of the AT

Synergistic effect

The synergistic effect provided by the addition of halide ions such as I⁻, Br⁻, and Cl⁻ to the solution containing 1M H_2SO_4 and the inhibitors (AT, CBT, NBT) was studied by weight loss method and the data are presented in Table 6. Analysis of the data reveals that the addition of halides to the inhibitors increases the inhibition at each concentration of the inhibitor tested. This increase in inhibition efficiency shows that the mechanism of the synergistic action is due to the co- adsorption of halides and the inhibitor. The strong chemisorptions of halide ions on mild steel surface make the iron surface to a negatively charged one. Organic compounds containing nitrogen in aqueous acidic solutions may exist either as neutral molecules or cations. The positively charged propagated cations may then be adsorbed by columbic attraction on the metal surface where halide ions are already adsorbed. This leads to more surface coverage and hence greater inhibition [11]. The order of synergism of halide ions with the tested

inhibitors has been found to be $I^- > Br^- > Cl^-$. The reason for better synergism with iodide ion is due to the large size and ease of polarisibility of I^- ion, which facilitates chemisorptions on the iron surface.
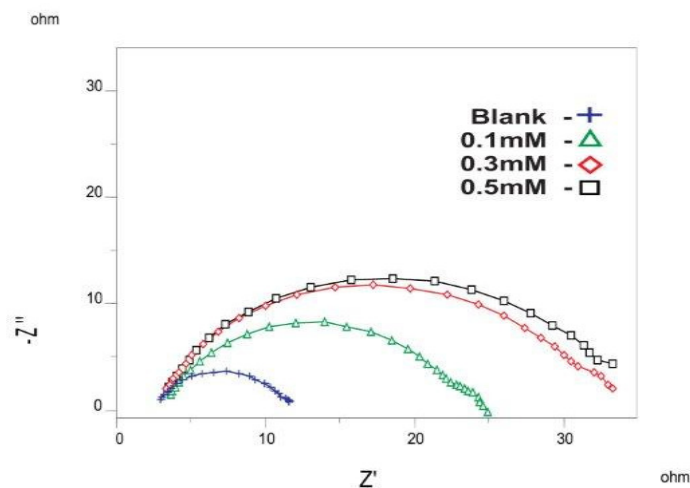

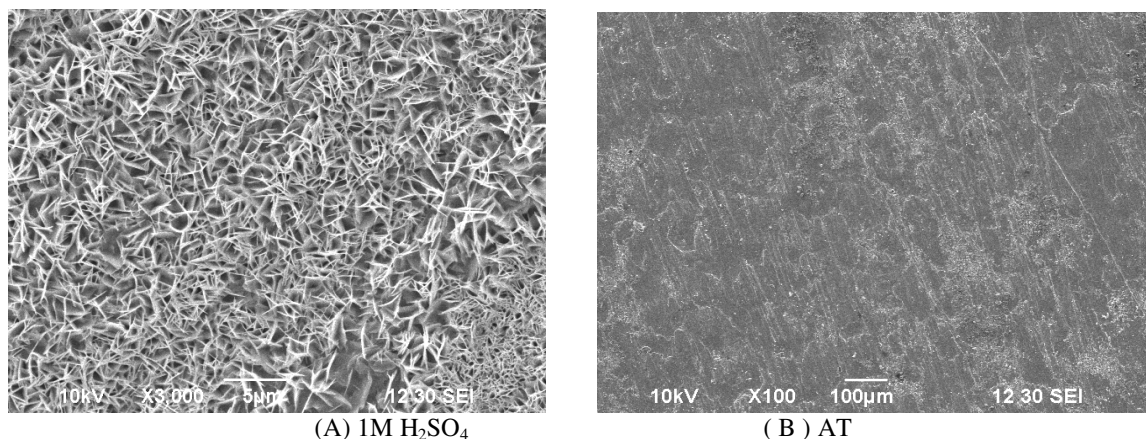Fig-5 : Nyquist diagram for mild steel in IM H_2SO_4 in presence and absence of the AT

(A) 1M H_2SO_4 (B) AT

Fig.-6: SEM images of steel samples; Absence of inhibitor (A), In H_2SO_4 medium at 0.5mM inhibitor (AT)(B)

Scanning electron microscopic studies
SEM photograph of the metal sample in the presence and absence of inhibitor AT is shown in Fig 6. Close examination of the SEM image revealed that the specimen immersed in the inhibitor solution is in better condition with smooth surfaces compared with those of corroded rough and coarse uneven surfaces of mild steel immersed in 1M sulphuric acid alone. This observation indicated that corrosion rate is reduced by the adsorption of inhibitor molecule on the metal surface as a protective layer [12].

Evaluation of inhibitors
Inhibition efficiency values obtained for the inhibitors by the three methods shows the following order-
                    AT>CBT>NBT
All the three inhibitors have the same molecular structure except for the substituents in the phenyl ring at the position 6 of the thiazines.
The best performance of AT may be attributed to the presence of electron releasing $-OCH_3$ group which enriches the electron density on the phenyl ring and provides an active adsorption centre. The lower

inhibition efficiency of CBT may due to the presence of electron withdrawing – Cl group. The very low inhibition efficiency shown by NBT is not only due to the presence of electron withdrawing NO_2 group, but also due to the reduction of NO_2 group in acidic medium in the presence of Fe. The evolved heat of hydrogenation may aid the desorption of the molecule from the steel surface and lowers the efficiency of the compounds. Similar results have been reported by Elewady et al for the nitro substituted pyrimidine derivatives [13].

CONCLUSION

i.   Thiazines act as good corrosion inhibitors for mild steel in 1M sulphuric acid.
ii.   The inhibition efficiency of the inhibitors increases with increase in concentration and decreases with increase in temperature.
iii.   The adsorption of the inhibitors obey Langmuir's adsorption isotherm.
iv.   The less negative value of ΔG^o_{ads} (<-40 KJ/mol) indicates the spontaneous and physical adsorption of the inhibitors on the metal surface.
v.   Addition of halide ions leads to pronounced increase in inhibition efficiency in which columbic attraction prevails.
vi.   The Tafel slopes obtained from potentiodynamic polarization study indicates that the inhibitors behave as mixed type.

REFERENCES

1. R.Kalirajan, S.U.Sivakumar, S.Jubie, B.Gowramma and B.Suresh, *Int. J. Chem Tech Research,* **1,** 27 (2009).
2. E.E.Ebenso, Hailemichael Alemu, S.A.Umoren and I.B.Obot, *Int.J.Electrochem.Sci.*, **3**,1325 (2008).
3. S. Chitra, K. Parameswari, M. Vidhya, M. Kalishwari, and A. Selvaraj, *Int. J. Electrochem. Sci.,* **6**, 4593 (2011).
4. U.Ergun, D.Yuzer, K.C.Emregul, *Mater. Chem.Phy.*, **109**, 492 (2008).
5. I.B.Obot, N.O. Obi – Egbedi, S.A. Umoren, E.E. Ebnenso, *Chem. Eng. Comm.***198,** 711 (2011).
6. I. Dehri, M. Ozcan, *Mater. Chem.Phy.*, **98**, 316 (2006).
7. M. I. Awad, *J.Appl.Electrochem.*, **36**, 1163 (2006).
8. R.Alberty. R. silbey, *Physical chemistry*, Second Edition, Wiley, New York, P.845 (1997).
9. F.w. Schapink, M. Oudeman, K.W. Leu, J.N. Helle, *Trans. Farad. Soc.* **56,** 415 (1960).
10. D.S. Shealty, P. Shetly, H.V.S. Nayak, *J. Chilean Chem. Soc.*, **51**, 849 (2006).
11. A.A. EL. Warraky and H.A. El. Dahan, *J. Mater.Sci*, **32**, 3693(1997).
12. R.A. Prabhu, T.V. Venkatesha, and A.V. Shanbhag, *J. Iran Chem. Soc.,* **6 (2)**, 353 (2009).
13. G.V. Elewady, *Int. J. Electrochem. Sci.*, **3**, 1149 (2008).

[RJC-984/2012]