*Research Journal of Chemical Sciences* ______________________________________________ ISSN 2231-606X
Vol. **5(2),** 59-63, February **(2015)** *Res. J. Chem. Sci.*

# Inhibitive action of 3-Hydroxy-3-(4methylphenyl-1-(4-sulphonato (sodium salt) phenyl triazene on Corrosion of Copper in HCl medium

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**Available online at: www.isca.in, www.isca.me**
Received 29th January 2015, revised 13th February 2015, accepted 17th February 2015

## Abstract

*Corrosion inhibition of copper in 1N HCl solution by 3-Hydroxy-3-(4-methylphenyl)-1-(4-sulphonato (sodium salt) phenyl) triazene (HPST) has been studied using weight loss techniques at temperatures ranging from 303 to 343 K. It is observed that the proposed organic compound exhibit 84.4% inhibition efficiency at 303 K temperature in 1N HCl solution . Increase the concentration of HPST inhibition efficiency increases whereas increase in temperature decreases inhibition efficiency. The inhibitior show maximum inhibition efficiency for 0.002 M concentration of HPST at 303 K temperature. Activation energy ($E_a$), Enthalpy (ΔH),Entropy (ΔS) and Gibbs free energy have also been reported. The Langmuir isotherm was found to accurately describe the adsorption behavior of the compound.*

**Keywords**: Corrosion inhibitor, copper, HCl medium, weight loss.

## Introduction

Copper is an important industrial metal having variety of application. It is used in electronic equipments. During many process like cleaning metal contact with acid.To prevent metal corrosion inhibitor are widely used. Many substuted heterocyclic compound, N, O, S, containing compound and double bond containing compound studied as inhibitors for corrosion[1-6]. Plant extracts are also use as inhibitor for corrosion[7-10]. The use of inhibitors is one of the most practical methods to protect copper from corrosion[11]. In our laboratory hydroxytriazenes have been explored as corrosion inhibitors for brass in ammoniacal medium[12]. In the present study 3-Hydroxy-3-(4methylphenyl -1-(4-sulphonato (sodium salt) phenyl triazene (HPST) has been studied for its corrosion inhibition against copper in 1N HCl solution.

## Material and Methods

**Synthesis of HPST** :- 3-Hydroxy-3-(4-methylphenyl)-1-(4-sulphonato (sodium salt) phenyl) triazene (HPST) is synthesized through three major steps as described below:

**Reduction of nitro compound:** In this step 0.03 moles of nitro benzene was reduced in the presence of $NH_4Cl$ (1.6 gm) in water- alcohol medium using mechanical stirrer at 50-60 °C to obtain phenyl hydroxylamine. The resulting mixture was further stirred for another 15 minutes at 60 °C to complete the reaction. It was filtered off and finally used for coupling process.

**Diazotization of amino compound:** In this step 0.03 moles of sulphanillic acid was diazotized with sodium nitrite (1.4 gm) at 0–5 °C in acidic medium under constant magnetic stirring to obtain p-sulphonatophenyldiazonium chloride.

**Coupling:** The phenyl hydroxyl amine from step-I was coupled with p-sulphonato phenyldiazonium chloride from step-II in sodium acetate buffer of medium of 5–6 pH at 0–5⁰C. Finally product of coupling was purified and re-crystallized with absolute alcohol. Purity of HPST was checked by TLC and melting point detection method and characterized by IR study, Elemental analysis, $^1$H NMR, and Mass analysis

**Metal Specimen and Methodology:** Copper sheet has been used to study the inhibition effect of HPST. Rectangular size specimen of copper sheet containing a small hole use for study inhibition study. Specimen were cleaned with the help of emery paper , carefully washed with water and acetone . Dried each specimen then weighed. Each specimen was suspended for 24 hours in a beaker containing 100 ml of test solution with and without different concentration of inhibitor. The specimens were taken out from the solution, washed with water and acetone then dried and weighed. The same experiment was repeated using various concentrations of HPST to record protection offered by HPST

**Weight Loss Measurement:** Weight loss of copper specimen before and after dipping in corrosion solution was calculated by usual method and percentage were calculated by using following formula[13]

$$I.E = \frac{W_0 - W}{W_0} \times 100 \quad (1)$$

Where: I.E. = Inhibition efficiency of HPST in 1N HCl solution, $W_0$ = Weight loss in solution without inhibitor, W = Weight loss in solution with different concentration of inhibitor.

The corrosion rate ($C_{Rate}$) in mg $cm^{-2}$ $h^{-1}$ was calculated from the following equation[14]

$$C_{Rate} = \frac{W_P - W_S}{At} \qquad (2)$$

Where: $W_p$ = Weight loss before immersion of test solution, $W_s$ = Weight loss after immersion of test solution, A = Total area of one copper sheet specimen, T=Immersion time

## Results and Discussion

The inhibition efficiency and corrosion rate ($C_{Rate}$) in 1N HCl solution at various concentration of the HPST was calculated using weight loss technique in absence and presence of different concentration of inhibitor. Calculated Values are reported in table-1.

Table-1: From table 1 it is clearly observed that increasing the concentration of inhibitor (HPST) inhibition efficiency increases where as corrosion rate decreases. Maximum inhibition 84.6% shown at 0.002 M concentration of inhibitor in 1N HCl solution.

**Effect of temperature:** The effect of temperature on inhibition efficiency was studied in temperature ranging 303 to 343. Corresponding observations are listed in table.

Figure-1: A graph is plotted between temperature and inhibition efficiency (IE) at temperature ranging 303 to 343 for different concentration of inhibitor. From figure 1, it is clearly observed that inhibition efficiency decreases with rise in temperature. This is due to decrease in adsorption of inhibitor molecule on copper surface that would suggest physical adsorption of HPST on copper surface. The activation energy of inhibition process can be calculated using Arrhenius equation[15]

$$\log C_{Rate} = A + \frac{-E_a}{RT} \qquad (3)$$

Where: $C_{Rate}$ = Corrosion rate, A =Arrhenious pre exponention factor, $E_a$ =Activation energy of corrosion reaction, R = Universal gas constant, T = absolute temperature.

Figure-2: Figure 2 represent the Arrhenius plot of log $C_{Rate}$ against 1/T for different concentration of inhibitor solutions. Graph shown straight line. By using slope (-Ea/RT), activation energy (Slope X 2.303 X R) was calculated. Increases the concentration of inhibitor (HPST) activation energy increases. The activation energy increased in the presence of HPST, which indicated physical adsorption (electrostatic) in the first stage. Other thermodynamic parameter

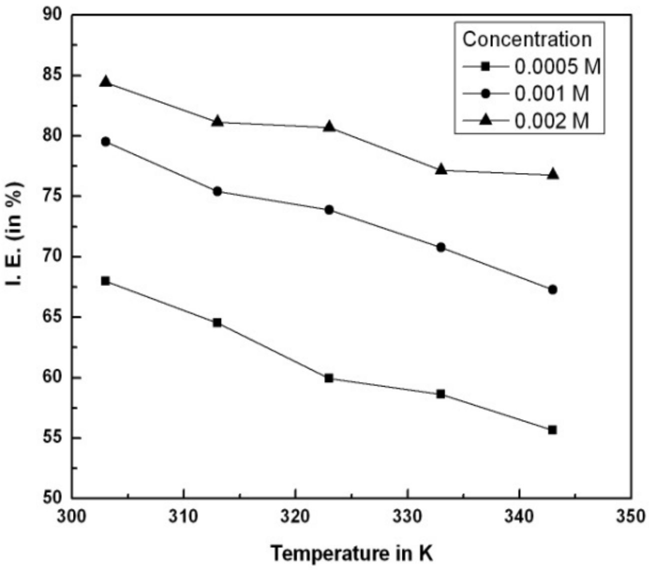


**Figure-1**
**Effect of temperature on IE**

Enthalpy (ΔH) and entropy (ΔS) of activation were calculated from the transition state theory[16]

$$C_{Rate} = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right) \qquad (4)$$

Where: $C_{Rate}$ = corrosion rate, h = Plank's constant, N = Avogadro's number, R = Universal gas constant, T = Absolute temperature.

Figure-3: Figure 3 shows the transition state plot for copper corrosion in 1N HCl in the absence and presence of different concentrations of HPST. The curve plotted between log $C_{Rate}$ against 1/T shown straight lines .Enthalpies and Entropies were calculated using slope and intercept of these lines. According to transition state theory Enthalpy (ΔH)=slope X 2.302X R and Entropy (ΔS)=2.303 X R(Intercept-log(R/Nh)). Calculated values of enthalpies and entropies listed in table-2.

Table-2: From table 2 it is clearly observe that ΔH values are positive and ΔS values are large and negative. Increasing concentration of inhibitor ΔH value move toward high positive value that show higher inhibition efficiency of inhibitor(HPST). Enthalpies increases with an increase in the concentration of HPST.

The entropy of activation, (ΔS) was negative both in the absence and presence of inhibitor. This indicate that in the rate determining step activated complex represents association rather than dissociation, indicating that ongoing reactant to the activated complex there is decrease in disorder[17].

**Table -1**
**Effect of concentration of HPST on Corrosion rate for copper in 1N HCl solution**

| Conc. of inhibitor (Mole) | 303(K) | | 313(K) | | 323(K) | | 333(K) | | 343(K) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $C_{Rate}$ | IE% | $C_{Rate}$ | IE% | $C_{Rate}$ | IE% | $C_{Rate}$ | IE% | $C_{Rate}$ | IE% |
| Blank | 0.081 | - | 0.116 | - | 0.234 | - | 0.350 | - | 0.473 | - |
| 0.0005 | 0.026 | 68.00 | 0.041 | 64.57 | 0.094 | 59.94 | 0.147 | 58.61 | 0.210 | 55.63 |
| 0.001 | 0.016 | 79.52 | 0.028 | 75.42 | 0.061 | 73.86 | 0.103 | 70.79 | 0.155 | 67.18 |
| 0.002 | 0.012 | 84.43 | 0.022 | 81.14 | 0.045 | 80.68 | 0.081 | 77.15 | 0.110 | 76.76 |

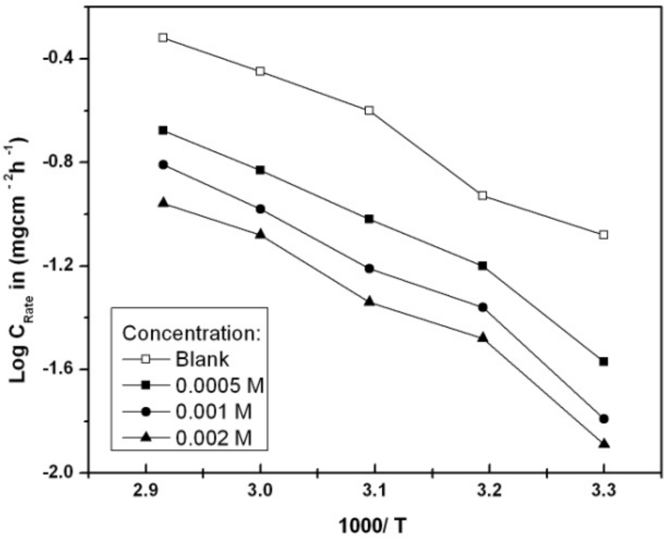


**Figure-2**
**Arrhenious Plot of Log $C_{Rate}$ against 1/T for copper (with and without solution of HPST)**

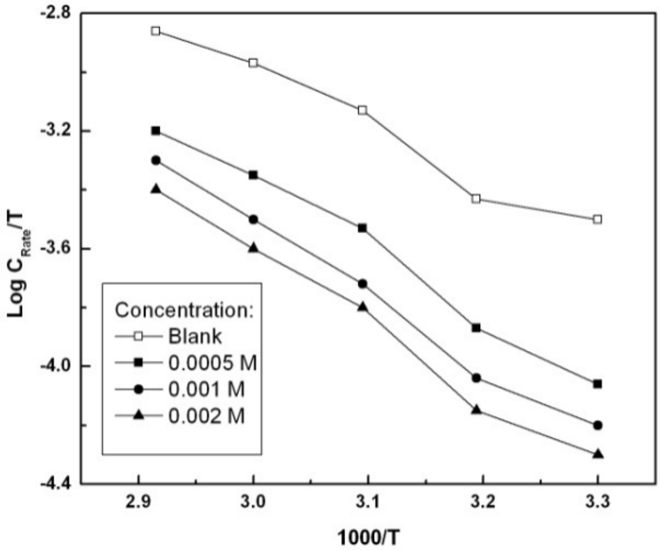


**Figure-3**
**Plot of log $C_{Rate}$/T verses 1000/T for different concentration of HPST**

**Table–2**
**Value of Enthalpy, Entropy and Activation energy at different concentration of inhibitor**

| Concentration in Mole | $E_a$ (KJ/mol) | ΔH (KJ/mol) | ΔS (J/Mol) |
|---|---|---|---|
| Blank | 39.51 | 34.43 | -150.80 |
| 0.0005 | 42.76 | 41.95 | -128.28 |
| 0.001 | 46.57 | 45.86 | -126.37 |
| 0.002 | 47.00 | 46.48 | -125.23 |

**Adsorption isotherm:** The interaction between metal surface and inhibitor can be explain by study of adsorption isotherm. Most commonly used isotherm are Frendlich,Langmuir, Frumkin.The experimental data was found to fit with Langmuir adsorption isotherm[18], which is express by

$$\frac{C}{\theta} = \frac{1}{k} + c \qquad (5)$$

Where: C=Inhibitor concentration at various temperature, K=Equillibrium constant for adsorption process, θ= Surface coverage, Surface coverage (θ) and inhibition efficiency have a direct relationship. The degree of surface coverage (θ) was evaluated from weight-loss measurements by use of the relationship[19]

$$\theta = \frac{IE\%}{100} \qquad (6)$$

Figure-4: The plot of log c/θ against concentration yield straight line. Linear fit was observed with regression coefficient 0.99 which suggest that the adsorption of inhibitor on copper surface follows Langmuir adsorption isotherm[20].

**Table 3**
**Value of Gibbs free energy at different temperature for HPST in 1N HCl solution**

| Temp(K) | $R^2$ | Slope | ΔG($KJmol^{-1}$) |
|---|---|---|---|
| 303 | 0.99 | 1.16 | -32.97 |
| 313 | 0.99 | 1.19 | -33.30 |
| 323 | 0.99 | 1.21 | -34.34 |
| 333 | 0.99 | 1.24 | -34.60 |
| 343 | 0.99 | 1.24 | -35.07 |

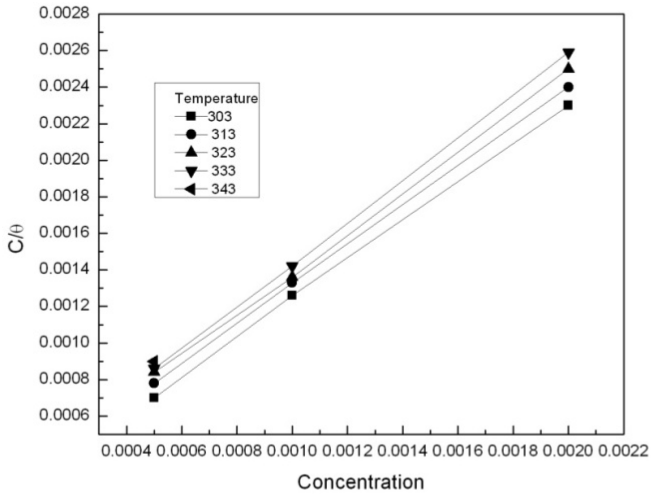


**Figure-4**
**Plot of C/θ against C for copper at different temperatures**

From the intercept K (equilibrium constant) was calculated which is related to Gibbs free energy of adsorption by following equation

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G}{RT}\right) \quad (7)$$

Table-3: Table-3 show the Value of ΔG calculated .The value of ΔG were large and negative which indicates that the adsorption of inhibitors on copper surface have spontaneous process.

## Conclusion

The results of experiment reveal that the compound HPST decreases the corrosion rate of copper in 1N HCl solution at constant temperature. IE increases with increase in inhibitor concentration, whereas at constant concentration IE decreases with increase temperature. From our study it is also concluded that the inhibitor shows maximum inhibition efficiency up to 84.4% which confirms that the inhibition occurs by adsorption according to the Langmuir isotherm.

## Acknowledgement

The authors would like to thank University Grants Commission (UGC), New Delhi for financial support in the form of JRF to one of the author (P.S.).

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