

## Selective Bis-N-aryl thiosemicarbazones as efficient corrosion inhibitors

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### ABSTRACT

The study of the effect of the Bis-N-aryl thiosemicarbazone compounds on the corrosion behaviour of mild steel in 1M sulphuric acid and in 1M hydrochloric acid shows that these compounds are very efficient inhibitors. Their inhibition efficiency increased with increase in concentration and also increased with temperature. The inhibitors showed a mixed type of inhibition in potentiodynamic polarization study and in impedance method in presence and absence of inhibitors. The adsorption of inhibition followed Langmuir adsorption isotherm. The thermodynamic parameters such as activation energy ( $E_a$ ) and free energy of adsorption  $G_{ads}$  were calculated. The  $E_a$  value of the uninhibited solution was less than the inhibited solutions revealing chemisorption of the inhibitor on the mild surface.

**Key words:** chemisorption, mild steel, thiosemicarbazone,  
Langmuir adsorption isotherm, mixed type.

### INTRODUCTION

Acid solutions are widely used in industries. The most important areas of application are acid pickling, industrial acid cleaning, acid descaling and oil well cleaning. Many nitrogen containing heterocyclic compounds with polar groups or  $\pi$  electrons are employed as good corrosion inhibitors for mild steel in acid media. Inhibition by these molecules is due to adsorption, which depends on the molecules and ions on the metal surface. The adsorption depends on the chemical structure of the inhibitors, type of the aggressive acid and the nature and the surface charge on the metal.

The aim of the present study is to synthesis various derivatives of arylthiosemicarbazone and to study the inhibition efficiency of these inhibitors on the corrosion process of mild steel in 1M sulphuric acid and 1M hydrochloric acid solutions. The inhibition efficiency has been evaluated by

weight loss, polarization and electrochemical techniques.

### MATERIAL AND METHODS

#### Materials and preparation

Mild steel strips (C-0.07%, S-nil, P-0.008%, Si-nil, Mn-0.34%, Fe-Rest) of size 3.5cm  $\times$  1.5cm  $\times$  0.056cm were used for weight loss. The same mild steel specimens were also used for electrochemical measurements having 0.785cm<sup>2</sup> as surface area. The surface of the specimens were polished successively with 1/0, 2/0, 3/0, 4/0 emery papers and are degreased with acetone and dried using hot air drier. The plates were then dried using hot air drier and then kept in a desiccators to avoid the absorption of moisture. Sulphuric acid and hydrochloric acid used were of L.R Grade and different concentrations of acid were prepared using double distilled water.

### Synthesis of inhibitors

Aryl thiosemicarbazones of various substituents have been synthesized under two stages. The first stage is the conventional method in which arylthiosemicarbazide were prepared by mixing aromatic amines with 95% ethanol and few ml of  $\text{NH}_4\text{OH}$ . After cooling the reaction mixture, few drops of  $\text{CS}_2$  and 0.1 mole of sodiumchloroacetate was added. Later few ml of hydrazine hydrate was added and the mixture was warmed and kept overnight. The product was filtered and dried. In the second stage, the arylthiosemicarbazide is mixed with respective aldehydes and the reaction is carried over microwave oven. The product formed was filtered, cooled and crystallized from ethanol.

### Weight Loss Method

The experiment was proceeded with both 1M  $\text{H}_2\text{SO}_4$  and then with 1M HCl. First 1M  $\text{H}_2\text{SO}_4$  acid solutions was prepared with distilled water and then taken in a 100 ml beaker and the specimens in triplicate were suspended in the solutions using glass hooks. After 3 hours, the specimens were removed washed with running water, dried and weighed. From the initial and the final weights of the specimen, loss in weight was calculated. Duplicate experiments were performed in each case.

### Electrochemical methods

#### Potentiodynamic polarization studies

Potentiodynamic polarization studies were carried out for the corrosion of mild steel with various concentration of inhibitors in 1M  $\text{H}_2\text{SO}_4$  and 1M HCl with and without inhibitors. The experiments were carried out at  $30 \pm 1^\circ\text{C}$  with a fine Luggin capillary to avoid ohmic polarization. The working electrode is prepared from a cylindrical mild steel rod insulated with Teflon tube such that the area exposed to the solution was  $0.75\text{cm}^2$ . A saturated calomel electrode was used as the reference and Platinum electrode of  $1\text{cm}^2$  was used as counter electrode. A graph was plotted with potential,  $E$  vs  $\log I$  and Tafel constant  $b_a$  and  $b_c$ ,  $E_{\text{corr}}$  (corrosion potential) and  $I_{\text{corr}}$  (corrosion current) were calculated.

#### Impedance measurements

The electrochemical impedance measurements were carried out using mild steel in 1M  $\text{H}_2\text{SO}_4$  and 1M HCl with and without inhibitor at  $30^\circ\text{C}$ . A plot of  $z'$  (real part of impedance) and

$z''$  (imaginary part of impedance) were made from which  $R_{\text{ct}}$  (charge transfer resistance),  $C_{\text{dl}}$  (double layer capacitance) and inhibition efficiency were calculated.

## DISCUSSION

### Weight Loss Measurements

The inhibition efficiency and corrosion rate of thiosemicarbazone compounds at 0.05mM, 0.1mM, 0.3mM, 0.6mM of the inhibitor in both 1M  $\text{H}_2\text{SO}_4$  and 1M HCl evaluated by weight loss experiment after 3hrs of immersion are given in table 1.

It has been observed that inhibition efficiency increases with increase in concentration and reaches a maximum of 98% at 0.06mM in 1M  $\text{H}_2\text{SO}_4$ . In HCl the range of inhibition efficiency is maximum >90% even at low concentration of 0.05mM proving efficient inhibition in HCl solution

The results showed that with the increase in concentrations of N-Aryl Thiosemicarbazones the metal loss is decreased to a considerable amount >95%. This is due to the fact that the inhibitors are adsorbed due to increased surface coverage.

The figure 3 revealed the fact that corrosion rate decreased with increase in concentration of the inhibitors in both HCl and  $\text{H}_2\text{SO}_4$  media.

### Potentiodynamic polarization studies

Polarization curve for mild steel in 1M  $\text{H}_2\text{SO}_4$  and 1M HCl for the inhibitor BVA is shown in figures 5 & 6.

The values of Tafel constant ( $b_a, b_c$ ), Corrosion potential, corrosion current are given in the table 7

The corrosion potential shifts towards a noble direction in the presence of inhibitors. The presence of inhibiting compounds has affected both anodic and cathodic Tafel slopes. Thus proving it to be a mixed inhibitors.

### Adsorption Isotherm

The probable mechanism of corrosion inhibition on mild steel by thiosemicarbazone may

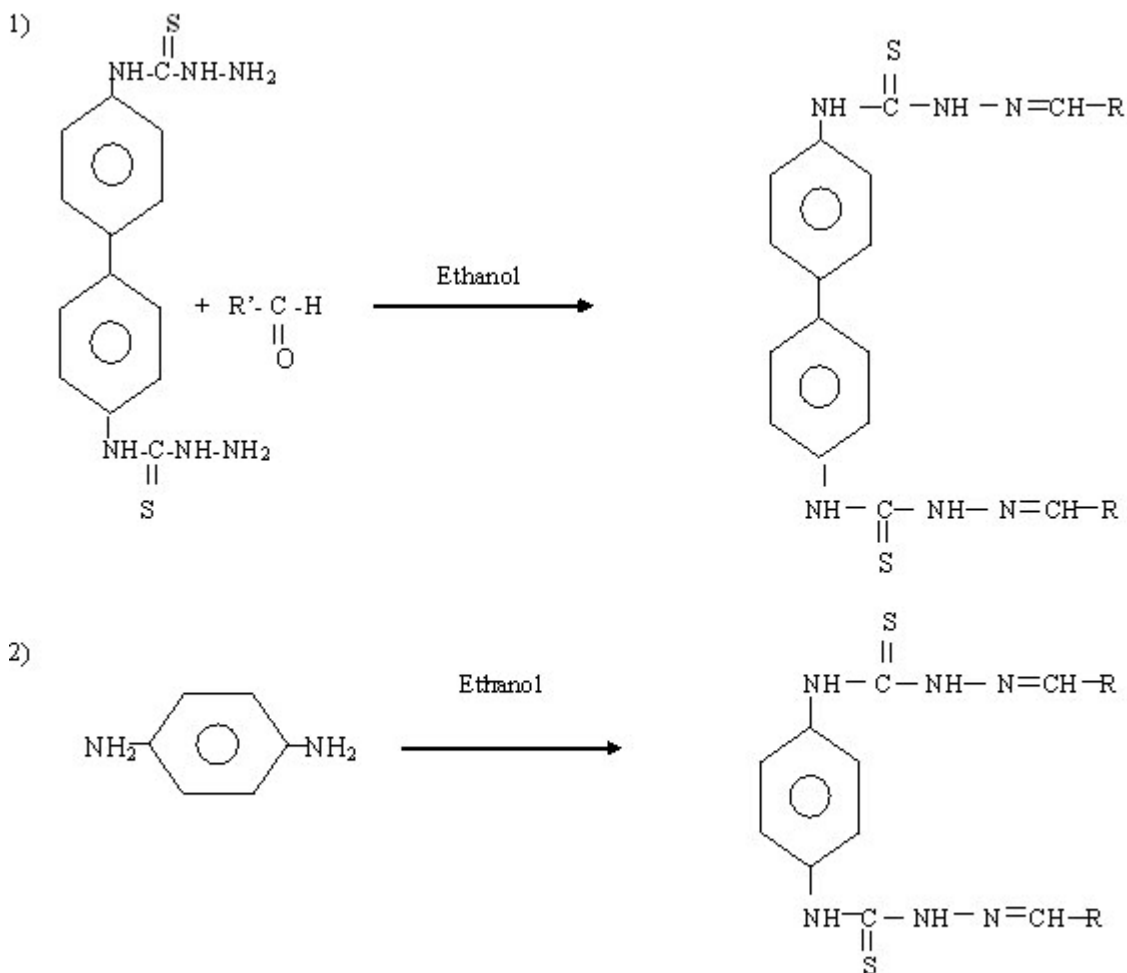
be deduced on the basis of adsorption. The adsorption depends on the chemical structure of the inhibitor, chemical composition of the solution, nature of the metal surface, temperature and electrochemical potential at the metal-solution interface.

Thiosemicarbazone compounds acted via simple adsorption model and exactly fit into the Langmuir adsorption isotherm by plotting  $\log(\theta/1-\theta)$  against  $\log$  concentration.

In case of heterocyclic compounds in acidic media mostly adsorption is ascribed to an effect connected with the aromatic rings. It was

reported by Granese(1) that the adsorption of heterocyclic compounds occurs with aromatic ring parallel to the metal surface. The degree of adsorption appears to depend mainly on the electronic structure of molecules.

Since there is an availability of nonbonded lone pair and  $\pi$  electron in thiosemicarbazone, this facilitates electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from thiosemicarbazone to the metal surface may be formed (2). The strength of chemisorptive bond depends on the electron density on the donor atom of the functional group and also on the polarizability of the group.



R =  $C_6H_2(OCH_3)_3CHO$  (3,4,5-trimethoxy benzaldehyde)  
 $C_6H_3(OCH_3)_2CHO$  (veratraldehyde)

| Name of the Compound   | Abbreviation | Strucutre   |
|--|--------------|---|
| Bis-N-(3,4,5-trimehtoxy  |              |   |
| benzaldehyde)-benzidine<br>thiosemicarbazones  | BVA          | <p>When R= C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>3</sub>CH-</p> |
| Bis-N-(3,4-dimehtoxy   |              |   |
| benzaldehyde)-<br>benzindinethiosemicarbazones<br>BBA When R= C <sub>6</sub> H <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> CH- |              |   |
| Bis-N-(3,4,5-trimehtoxy<br>benzaldehyde)-p-phenylene<br>diamine thiosemicarbazones   | PVA          | <p>When R= C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>3</sub>CH-</p> |
| Bis-N-(3,4-dimehtoxy benzaldehyde)   |              |   |
| -p-Phenylene<br>diaminethiosemicarbazones  | PBA          | <p>When R= C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>CH-</p> |
| Name of the Compound   | Abbreviation | Strucutre   |
| Bis-N-(3,4,5-trimehtoxy benzaldehyde)  | BVA          |   |
| -thiosemicarbazones  |              |   |

**Table 1: Inhibition efficiencies at various concentration of inhibitors for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> obtained from weight loss at room temperature**

| Name of the Inhibitor | Concentration in mM | Inhibition efficiency(%) | Corrosion rate(mpy) | Surface Coverage (θ) |
|-----------------------|---------------------|--------------------------|---------------------|----------------------|
| BVA                   | 0.05                | 41.12                    | 1181.82             | 0.4112               |
|                       | 0.1                 | 89.28                    | 215.20              | 0.8928               |
|                       | 0.3                 | 97.84                    | 43.33               | 0.9784               |
|                       | 0.6                 | 99.06                    | 18.78               | 0.9906               |
| BBA                   | 0.05                | 24.80                    | 1633.50             | 0.2480               |
|                       | 0.1                 | 84.77                    | 330.74              | 0.8477               |
|                       | 0.3                 | 96.41                    | 77.99               | 0.9641               |
|                       | 0.6                 | 97.74                    | 49.11               | 0.9774               |
| PVA                   | 0.05                | 78.09                    | 498.28              | 0.7809               |
|                       | 0.1                 | 92.19                    | 177.65              | 0.9219               |
|                       | 0.3                 | 98.22                    | 40.44               | 0.9822               |
|                       | 0.6                 | 99.17                    | 18.78               | 0.9917               |
| PBA                   | 0.05                | 65.05                    | 667.27              | 0.6505               |
|                       | 0.1                 | 91.83                    | 155.98              | 0.9183               |
|                       | 0.3                 | 97.23                    | 51.99               | 0.9723               |
|                       | 0.6                 | 98.33                    | 31.77               | 0.9833               |

**Table 2: Inhibition efficiencies at various concentration of inhibitors for the corrosion of mild steel in 1M HCl obtained from weight loss at room temperature**

| Name of the Inhibitor | Concentration in mM | Inhibition efficiency(%) | Corrosion rate(mpy) | Surface Coverage (θ) |
|-----------------------|---------------------|--------------------------|---------------------|----------------------|
| BVA                   | 0.05                | 87.88                    | 96.77               | 0.8788               |
|                       | 0.1                 | 92.40                    | 60.66               | 0.9240               |
|                       | 0.3                 | 94.94                    | 40.44               | 0.9494               |
|                       | 0.6                 | 96.02                    | 31.77               | 0.9602               |
| BBA                   | 0.05                | 87.88                    | 96.77               | 0.8788               |
|                       | 0.1                 | 92.40                    | 60.66               | 0.9240               |
|                       | 0.3                 | 94.94                    | 40.44               | 0.9494               |
|                       | 0.6                 | 96.02                    | 31.77               | 0.9602               |
| PVA                   | 0.05                | 93.52                    | 30.33               | 0.9352               |
|                       | 0.1                 | 95.37                    | 21.66               | 0.9537               |
|                       | 0.3                 | 96.30                    | 17.33               | 0.9630               |
|                       | 0.6                 | 98.46                    | 7.22                | 0.9846               |
| PBA                   | 0.05                | 90.27                    | 118.43              | 0.9027               |
|                       | 0.1                 | 93.24                    | 82.32               | 0.9324               |
|                       | 0.3                 | 97.27                    | 33.22               | 0.9727               |
|                       | 0.6                 | 98.10                    | 23.11               | 0.9810               |

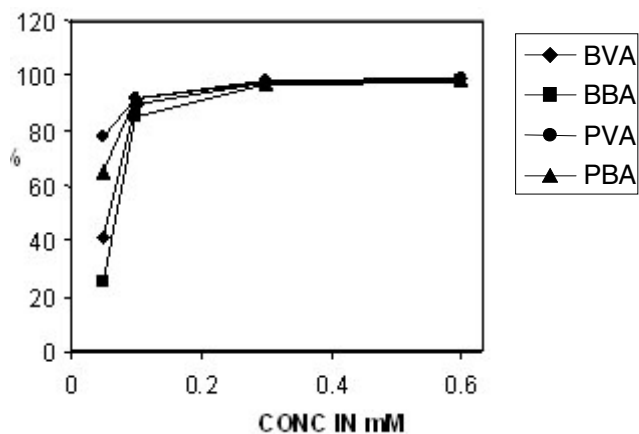


Fig. 1: Inhibition efficiency Vs concentration in 1M H<sub>2</sub>SO<sub>4</sub>

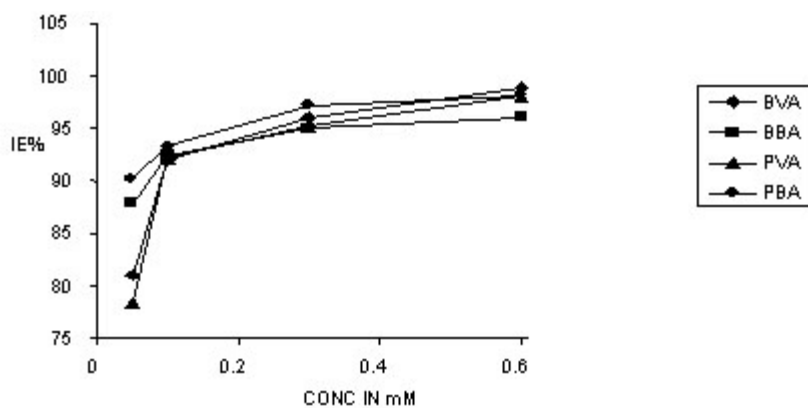


Fig. 2: Inhibition efficiency Vs concentration in 1M HCl

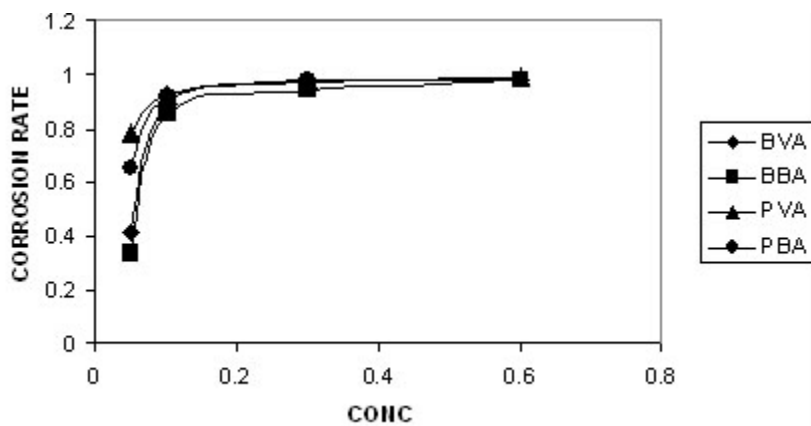


Fig. 3: Corrosion Rate Vs Conc for all Inhibitors in 1M H<sub>2</sub>SO<sub>4</sub>

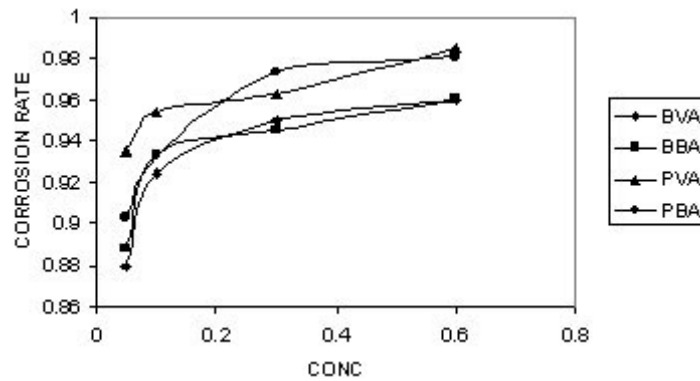


Fig. 4: Corrosion Rate Vs Concentration for all Inhibitors in 1M HCl

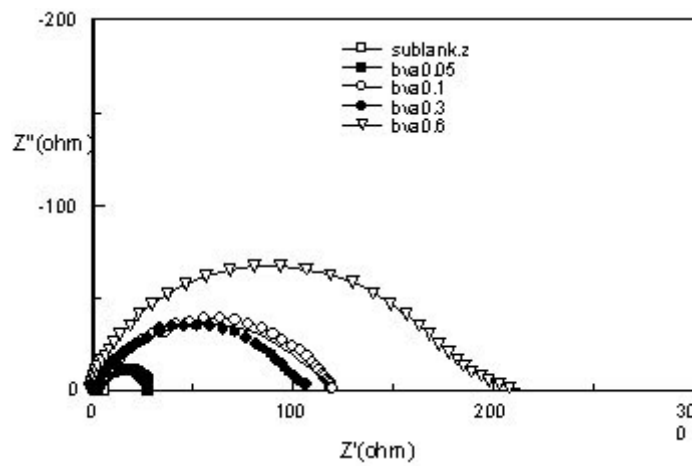


Fig. 5: Nyquist plots for mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of BVA

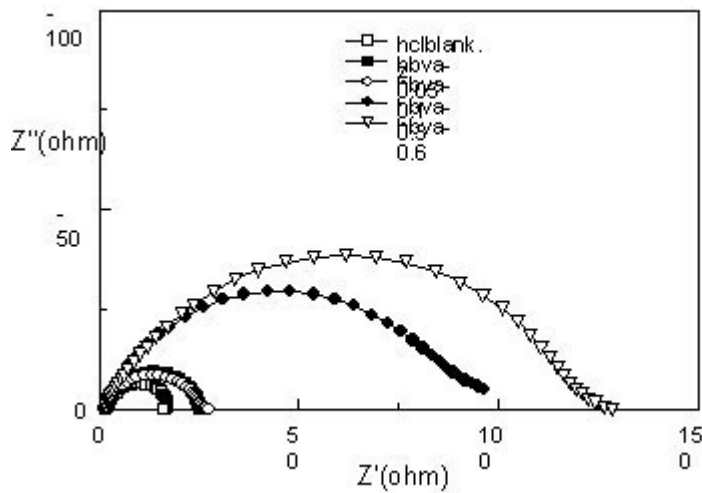


Fig. 6: Nyquist plots for mild steel in 1 M HCl in the absence and presence of BVA

Since nitrogen atom has higher electron density as compared to the oxygen and also sulphur which is most electronegative than nitrogen are present in thiosemicarbazone, the free unshared electrons are found to act as reaction centres of organic molecules which reacts with the metal surface(3).



### Effect of Temperature

The temperature dependence of the inhibition efficiency and also on comparing the values of effective  $E_a$  of the corrosion processes gives us the most important conclusions regarding the mode of adsorption and the mechanism of inhibiting action of the thiosemicarbazone inhibitors.

The effect of temperature on the corrosion behaviour of mild steel in presence and absence of the inhibitor were studied using weight loss technique. The corrosion rate of the inhibitors increases with increase in temperature. Temperature increase leads to the variation in effective activation

energy which would be higher in inhibitors absence. This is an indication that an adsorptive film of electrostatic character is formed which is obtained from the Arrhenius equation  $\log(\text{Rate}) = -E_a/T$  i.e. log of corrosion rate is a function of  $1/T$ . The values of activation energy  $E_a$  obtained from the slope of the Arrhenius plot. Negative values of  $\Delta G_{\text{ads}}^0$  point out the spontaneity of the adsorption process in the experimental conditions. Generally, values of  $\Delta G_{\text{ads}}^0$  until -20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal surface (physical adsorption). Those more negative than -40 kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption)[4,5,6].

In the present study the  $\Delta G_{\text{ads}}^0 > -20$  kJ/mol conforms that the adsorption of the inhibitor took place by chemisorption on the metal surface. Also activation energy decreases in inhibited solutions, this shows that a chemisorptive bond is formed between the organic inhibitor molecule and the metal surface.

**Table 7: Potentiodynamic polarization parameters for the corrosion of mild steel in 1 M  $H_2SO_4$  with and without Inhibitor**

| Name of the inhibitor | Inhibition concentration (mM) | $I_{\text{corr}}$ (mA/cm <sub>2</sub> ) $\times 10^{-4}$ | $E_{\text{corr}}$ (mV vs SCE) | $b_a$ (mV/dec) | $b_c$ (mV/dec) | Inhibition efficiency (%) |
|-----------------------|-------------------------------|--|-------------------------------|----------------|----------------|---------------------------|
|                       | BLANK                         | 77   | -0.5920                       | 184.67         | 206            | -                         |
| BVA                   | 0.05                          | 6.795  | -0.5765                       | 81.44          | 135.84         | 90.91                     |
|                       | 0.1                           | 1.375  | -0.5509                       | 67.39          | 118.91         | 98.31                     |
|                       | 0.3                           | 0.730  | -0.5329                       | 51.57          | 103.31         | 99.09                     |
|                       | 0.6                           | 0.318  | -0.5199                       | 45.38          | 99.492         | 99.61                     |
| BBA                   | 0.05                          | 11.47  | -0.5766                       | 91.67          | 149.44         | 85.71                     |
|                       | 0.1                           | 3.491  | -0.5639                       | 68.35          | 113.88         | 95.45                     |
|                       | 0.3                           | 0.372  | -0.5341                       | 49.09          | 98.58          | 99.61                     |
|                       | 0.6                           | 0.239  | -0.5189                       | 61.34          | 106.19         | 99.70                     |
| PVA                   | 0.05                          | 17.91  | -0.5695                       | 98.08          | 164.14         | 76.75                     |
|                       | 0.1                           | 5.043  | -0.5553                       | 69.91          | 130.56         | 93.50                     |
|                       | 0.3                           | 0.968  | -0.5374                       | 56.70          | 107.61         | 98.75                     |
|                       | 0.6                           | 0.431  | -0.5191                       | 46.27          | 92.55          | 99.44                     |
| PBA                   | 0.05                          | 22.926   | -0.5705                       | 104.76         | 164.94         | 70.26                     |
|                       | 0.1                           | 14.239   | -0.5671                       | 94.758         | 158.22         | 81.56                     |
|                       | 0.3                           | 2.345  | -0.5409                       | 60.384         | 115.38         | 97.01                     |
|                       | 0.6                           | 0.750  | -0.5265                       | 51.504         | 100.06         | 99.03                     |



### Nature of the inhibitor

In Sulphuric acid solutions, the inhibition efficiency calculated by impedance and polarization studies for the inhibitors exhibit a very high efficiency even at low concentration of about 0.05mM of the inhibitor. As the concentration of the inhibitor increases the inhibition efficiency increases from 50% to 98% at 0.6mM. The high inhibition efficiency or low corrosion rate of the inhibitors is explained by the fact that there are 6 electron donating  $-OCH_3$  groups attached to the benzene ring of the Aryl thiosemicarbazone I and III while 4 electron donating  $-OCH_3$  groups in II and IV Aryl thiosemicarbazone which facilitates the lone pair of electrons on nitrogen to block the corrosion site on the metal more efficiently. It is the lone pair of electron on the entire nitrogen atom which favours the inhibition process by chemisorption.

Chemisorption process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type of a bond. This is possible in case of a positive as well as a negative charge of the surface. The presence of a transition metal, having vacant, low energy electron orbital and of an inhibitor with molecules having relatively loosely bound electron or hetero atoms with lone pair electrons is necessary (9,10). Thus the presence of 6 nitrogen atoms in the inhibitor makes it chemically adsorbed on the metal surface.

Inhibition efficiency of the inhibitor is found to be greater in sulphuric solution. This may be due to the availability of more sites on the metal surface in the sulphuric acid solution because of lesser adsorption of the sulphate ions on the steel surface. In hydrochloric acid solution the inhibition efficiency varies from a negative inhibition efficiency to an

optimum of 85% at 0.6mM. This shows that corrosion rate of Aryl thiosemicarbazone are less in sulphuric acid compared to hydrochloric acid.

### CONCLUSIONS

1. N-Aryl thiosemicarbazones shows a high efficiency towards corrosion of mild steel in both 1M  $H_2SO_4$  and 1M HCl media with increase in concentration.
2. It shows higher efficiency in 1M HCl even at low concentration compared to 1M  $H_2SO_4$ .
3. The inhibition of corrosion by N-Aryl thiosemicarbazone is due to the chemical adsorption on the metal surface.
4. The activation energy decreases in the inhibited solution compared to uninhibited solution confirming that chemisorptive bond is formed.
5. The value of  $\Delta G > -20$  KJ/mol which also confirms that mode of adsorption is chemisorptive.
6. The corrosion rate decreases with increase in temperature which is a solid proof for the chemisorptions to be taken place.
7. The high efficiency of N-Aryl thiosemicarbazones is facilitated due to the electron donating  $-OCH_3$  group on the nitrogen which blocks the corrosion rate on the metal more efficiently.
8. The adsorption of inhibitors on mild steel in both 1M  $H_2SO_4$  and 1M HCl media obeys Langmuir adsorption.
9. The variation of Tafel constants  $b_a$ ,  $b_c$  and  $E_{corr}$  values with the increase in concentration of the inhibitors suggest that N-Aryl thiosemicarbazones act as mixed type of inhibitor.

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