

## CHAPTER - 7

### EFFECT OF CHANGE IN THE ANION OF THE AGGRESSIVE MEDIUM ON THE INHIBITIVE INFLUENCE OF ISOXAZOLINES, PYRAZOLINES, PYRIMIDINES AND BIS-DERIVATIVES

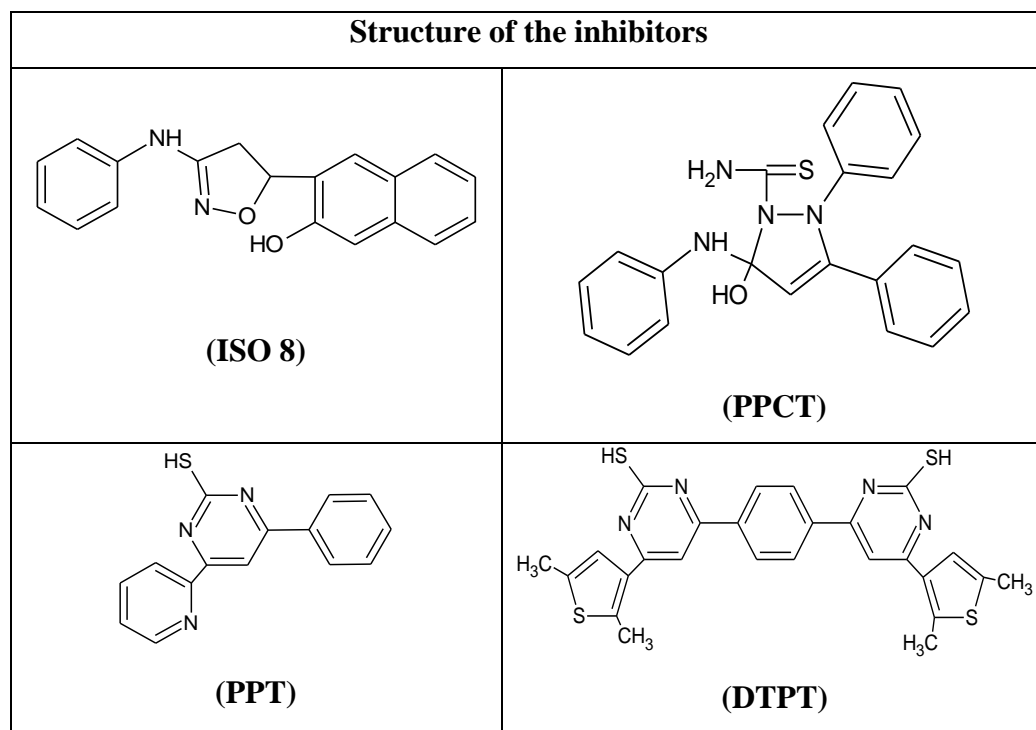
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#### 7.1 INTRODUCTION

Metal surfaces are extensively used in a variety of industrial applications such as petroleum, textile and marine industries as a component of pumps or valves that carry various types of substances. However some of these substances are highly corrosive and include such solutions as hydrochloric acid<sup>1</sup>. For instance, in the petroleum industry hydrochloric acid solutions are widely utilized for oil well acidizing, while in marine industries hydrochloric acid is largely used for pickling purposes<sup>2</sup>.

One of the most important applications of hydrochloric acid is its use in the pickling of iron and steel materials to remove rust or iron oxide scale from surface before subsequent processing such as extrusion, rolling galvanizing *etc.*. Based on the above views, some of the synthesized organic compounds namely 3-phenylamino-5-(2'-hydroxy naphthyl) isoxazoline (ISO 8), 5-hydroxy-2,3-diphenyl-5-(phenylamino)-2,5-dihydro-1*H*-pyrazole-1-carbothioamide (PPCT), 4-phenyl-6-(pyridin-2-yl)pyrimidine-2-thiol (PPT) and 5-(2,5-dimethylthiophen-3-yl)-4-(4-(6-(2,5-dimethylthiophen-3-yl)-2-mercaptopyrimidin-4-yl) phenyl) pyrimidin-2-thiol (DTPT), which exhibited excellent inhibition efficiency in 1M sulphuric acid medium have been chosen for study in 2M HCl. The present work was designed to compare the effect of these heterocyclic compounds as inhibitors for corrosion of mild steel in 2M hydrochloric acid solution using weight loss and electrochemical techniques. The molecular structures of the investigated compounds are as follows



## 7.2 RESULTS AND DISCUSSION

The effect of the addition of inhibitors (ISO 8, PPCT, PPT and DTPT) to 2M HCl at various concentrations on mild steel corrosion at 303 K after 3 hour immersion was studied by weight loss and electrochemical measurements. Corrosion parameters such as inhibition efficiency (%), corrosion rate (CR) and surface coverage ( $\theta$ ) at various concentrations of the inhibitors are given in Table 7.1. It is observed from Table 7.1 that at 303 K the inhibition efficiency increased and the corrosion rate decreased on increasing the concentration of the inhibitors. This may be due to the adsorption of the inhibitor molecules on the mild steel surface leading to the formation of a smooth layer on metal surface which prevents the contact of metal with the surrounding acidic environment. The higher bonding ability of the inhibitor molecules on the surface of mild steel may be due to the lone pair of electrons on hetero atoms and  $\pi$ -orbital character of the aromatic rings<sup>3</sup>.

The results obtained from electrochemical impedance technique in the absence and presence of selected concentration of inhibitors at 303 K is summarized in Table 7.2. The impedance spectra of mild steel recorded in 2M HCl are depicted as Nyquist plots as shown in Figs. 7.1 a-d. A considerable increase in the total impedance was observed due

to the addition of inhibitors. From the Figs. 7.1 a-d, it is evident that impedance response of mild steel has significantly changed after the addition of inhibitors to the corrosive medium, due to increase in substrate impedance, which is attributed to an increase in the concentration of the inhibitors. In the presence of inhibitors (ISO 8, PPCT, PPT and DTPT) comparing with the blank system, the shape was maintained throughout all selected concentrations, indicating that there was almost no change in the corrosion mechanism due to inhibitor addition. These capacitive loops are not perfect semicircles, which can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneties of the mild steel electrode surface<sup>4</sup>. There was a gradual increase in the diameter of each of the semicircles of the Nyquist plots when the concentration increases. This gradual increase of the diameters corroborated that the  $R_{ct}$  values increased upto the highest concentration of the selected inhibitors.

It is observed from Table 7.2, that  $R_{ct}$  values increased and  $C_{dl}$  values decreased with increase in concentration of the inhibitors. This may be due to the increase in the surface coverage on the mild steel by the inhibitor molecules, which lead to an increase in inhibition efficiency. The  $C_{dl}$  is related to the thickness of the protective layer ( $d$ ) by the following equation<sup>5</sup>.

$$C_{dl} = \frac{\epsilon\epsilon_0 A}{d} \longrightarrow 7.1$$

where  $\epsilon$  is the dielectric constant of the medium,  $\epsilon_0$  is the permittivity of the free space and  $A$  is the effective surface area of the electrode. The decrease in  $C_{dl}$  leads to an increase in thickness of the double layer, which confirmed that the inhibitor molecules inhibit the corrosion by adsorption at the mild steel-solution interface. The changes in  $C_{dl}$  values are due to the replacement of water molecules by the inhibitors.

The potentiodynamic polarization curves obtained in the absence and presence of inhibitors (ISO 8, PPCT, PPT, DTPT) are shown in Figs. 7.2 a-d. The electrochemical parameters such as corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ) and Tafel slopes ( $b_c$  and  $b_a$ ) obtained from the polarization measurements are given in Table 7.3. The change in the values of the electrochemical parameters gives the possibility of estimating the influence of the inhibitors on the corrosion process kinetics. It is clear from Table 7.3 that the values of inhibition efficiency increased with increase in the

concentration of the inhibitors. This study has indicated that by increasing the inhibitor concentration, the corrosion current density ( $I_{\text{corr}}$ ) decreased and the corrosion potential ( $E_{\text{corr}}$ ) shifted slightly to more positive values.

It can be clearly seen from Figs. 7.2 a-d, that the addition of inhibitors to the corrosive solution reduces both anodic dissolution of mild steel and retards cathodic hydrogen evolution reactions. These results are indicative of the adsorption of the inhibitor molecules on the mild steel surface. The inhibition of both anodic and cathodic reactions was more and more pronounced with increasing inhibitor concentration, while the corrosion potential nearly remained the same in comparison with the corrosion potential observed in blank solution<sup>6, 7</sup>. The variation of the cathodic Tafel slope ( $b_c$ ) influenced the kinetics of the hydrogen evolution reaction. This also indicates an increase in the energy barrier for proton discharge, leading to less gas evolution. Further the shift in the anodic Tafel slope ( $b_a$ ) may be due to the adsorption of chloride ions or inhibitor molecules on the steel surface<sup>8</sup>. The presence of inhibitors did not prominently shift the corrosion potential, which confirms that the studied derivatives acted as mixed type. In 2M HCl solution,  $E_{\text{corr}}$  shifts to positive, which indicates that inhibitor molecules are more adsorbed on the anodic sites, resulting in an inhibition of the anodic reactions. Generally, if the displacement in  $E_{\text{corr}}$  is  $> 85$  mV with respect to  $E_{\text{corr}}$  in uninhibited solution, the inhibitor can be seen as a cathodic or anodic type. In our study, the maximum displacement is 48.8 mV for ISO 8, 48 for PPCT, 36.5 for PPT and 28 for DTPT respectively, which indicates that ISO 8, PPCT, PPT and DTPT can be arranged as mixed type inhibitors. Furthermore, in the presence of either compound, the slight change of both  $b_a$  and  $b_c$  indicates that the corrosion mechanism of mild steel does not change. These results prove that these inhibitors acted by simple blocking of the available surface area<sup>9</sup>. In other words, these inhibitors decreased the active surface area for the acid corrosion attack without affecting the mechanism of corrosion and caused inactivation of only a part of the metal surface with respect to the corrosive medium.

### **7.3 Comparison of inhibition efficiency of the inhibitors in 1M H<sub>2</sub>SO<sub>4</sub> and 2M HCl**

The % IE of the inhibitors at maximum concentration (10 mM for ISO 8, PPCT and 1mM for PPT, DTPT) studied by electrochemical and non-electrochemical techniques are presented in Table 7.4. Analysis of the data in Table 7.4 clearly reveals

that the inhibitors perform well in 2M HCl. From this observation it may be concluded that the inhibitors are more equally efficient in hydrochloric acid and in sulphuric acid, but slightly better in 2M HCl. Comparison of  $I_{\text{Corr}}$  values in the two systems reveals that chloride ions themselves have functioned as inhibitors by strongly interacting with the metal surface. The stronger specific reactant adsorption of chloride ions in HCl medium as compared to the  $\text{SO}_4^{2-}$  ions of sulphuric acid medium is also evident from the higher  $C_{\text{dl}}$  value ( $64.25 \mu\text{F cm}^{-2}$ ) in HCl in comparison to the lower  $C_{\text{dl}}$  value ( $36.6 \mu\text{F cm}^{-2}$ ) in sulphuric acid. This would ultimately mean that while in hydrochloric acid the chloride ions have worked in co-ordination with the inhibitor molecule through joint adsorption for the inhibition of corrosion and hence have played a major role in the process of inhibition.  $\text{SO}_4^{2-}$  ions of sulphuric acid have only played a weaker role and the role of inhibitor is important. The greater role of  $\text{Cl}^-$  ions of HCl medium in deciding the higher inhibition efficiency through the reactant adsorption as compared to  $\text{SO}_4^{2-}$  ions can be explained by considering the role of potential of the metal surface and the position of potential of zero charge on adsorption of inhibitors:-

It has been noticed by several authors that potential developed or applied on a metal surface decides the extent of adsorption of organic molecules and in this the anions of the aggressive medium plays the deciding role. For instance, **Hilson** has observed that the maximum adsorption of hexyl ammonium ions on iron surface in HCl medium takes place at potentials closer to  $-0.64 \text{ V/SCE}$  and when the potential is shifted to  $-0.44$  to  $-0.39 \text{ V/SCE}$ , these organic cations are desorbed<sup>10</sup>. **Bockris et al** have also observed that the adsorption of decyl amine and naphthal amine on iron group of metals in acidic medium clearly depends on the electrode potential<sup>11,12</sup>.

How does the potential of the metal surface affect the adsorption of organic molecules?

According to several investigators the shift or difference in the potential of metal surface relative to potential of zero charge  $\phi_n$  decides the nature of surface charge of the metal surface which ultimately decides the extent of adsorption of inhibitor molecules. Several theories have been proposed for the shift in the  $\phi_n$  relative to surface potential and vice versa. It has been proposed by **Bockris et al**<sup>11-12</sup> that the shift of the potential of maximum adsorption ( $\phi_m$ ) of iron relative to the potential of zero charge  $\phi_n = -0.47$  is due

the differences in the  $-\Delta G_{\text{ads}}$  of water molecule dipoles at positive and negative charges of the electrode. By exploiting the adsorption data on the positive side of stationary potential  $\phi_n$  **Damaskin et al** have shown that the shift of potential of maximum adsorption is influenced by adsorbed hydrogen and metal oxidation products on the adsorption of organic molecules<sup>13</sup>. These authors have also found that not only the adsorption of organic substances depends on the metal surface potential but also it is found to be maximum at potentials close to  $\phi_n$ .

Although several concepts have been proposed for the cause of shifts of surface potential and the potential of zero charge, the one proposed by **Frumkin**<sup>14</sup> and **Iofa**<sup>15</sup> seems to be more acceptable, which explains the difference between the inhibition behaviour of dianils in HCl and H<sub>2</sub>SO<sub>4</sub>. According to **Frumkin** and **Iofa** the increase in the adsorption of organic cations on going from sulphuric acid to halic acids as noticed by several authors<sup>16-19</sup> can be attributed to the changes in the surface charge of the metal in the presence of halide ions. The surface of iron is originally positively charged in 1N H<sub>2</sub>SO<sub>4</sub> at an open circuit potential of -0.48 to 0.51 mV/SCE and hence the ions of the like charges (cations) are not effectively adsorbed on the iron surface. When the halide ions are chemisorbed specifically on the metal surface, they actually enter into the metal part of the double layer and thereby shift the  $\phi_n$  toward more positive potentials. This renders the metal surface, at the open circuit potential, negatively charged and the cations are attracted by electrostatic forces to the metal surface. On the other hand, the SO<sub>4</sub><sup>2-</sup> ion of H<sub>2</sub>SO<sub>4</sub> enter only to the ionic part of the double layer due to weak adsorption and hence the shift in  $\phi_n$  is not as prominent in HCl medium or practically no shift in H<sub>2</sub>SO<sub>4</sub> and the surface may remain positively charged. This accounts for the stronger adsorption of organic cations and onium compounds in HCl than in H<sub>2</sub>SO<sub>4</sub>. **Damaskin et al**<sup>13</sup> have agreed with the concept of Frumkin and Iofa and have attributed the increased adsorption of organic cations in 1N HCl to the shift of  $\phi_n$  to more positive potentials to the irreversible chemisorption of Cl<sup>-</sup> ions.

Recent findings on the comparative performance of inhibitors in HCl and H<sub>2</sub>SO<sub>4</sub> media are in agreement with the conclusions derived by **Frumkin**<sup>14</sup>, **Iofa**<sup>15</sup> and **Damaskin et al**<sup>13</sup>. **Bentiss et al**<sup>20</sup>, **Rengamani et al**<sup>21</sup> and **Muralidharan et al**<sup>22</sup> have investigated thiadiazoles, aromatic amines, amino phenols and aminobenzoic acids

respectively in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> and made similar conclusions on the difference in the behaviour of inhibitors in these two acidic media. According to these authors these inhibitors exist in either as neutral molecules or in the form of protonated cations. The neutral molecules adsorb on the metal surface due to the sharing of lone pair of electrons on nitrogen atoms and the metal surface. The cationic inhibitor molecules electrostatically interact with the negatively charged metal surface though the positive charge on the nitrogen atom. Due to smaller degree of hydration, chloride ions are specifically strongly adsorbed and thereby create excess negative charge towards cationic inhibitor molecules in solution which are strongly adsorbed. However, the SO<sub>4</sub><sup>2-</sup> ions with high degree of hydration are weakly adsorbed in general and have little space for organic molecules to adsorb. Hence, higher synergistic inhibition is expected for anion of Cl<sup>-</sup> type. For the reason stated above the adsorption is greater from 2M HCl solutions than from 1M H<sub>2</sub>SO<sub>4</sub>, which leads to slightly higher inhibition efficiency values in HCl medium for ISO 8, PPCT, PPT and DTPT.

In tune with the earlier and recent findings the following conclusion can be made for the better performance of ISO 8, PPCT, PPT and DTPT in 2M HCl than in 1M H<sub>2</sub>SO<sub>4</sub>. For this purpose the general mechanism of inhibition proposed for the isoxazolines in Chapter - 3 of this thesis is to be recalled.

As per the proposed mechanism in acidic media, these compounds exist both as neutral molecules as well as their protonated counter parts. Adsorption occurs involving both the species but it is predominantly electrostatic. The Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> ions are first adsorbed on to the metal. Neutral species are adsorbed on free surface sites wherever possible. The adsorption of the protonated cationic species occurs through the joint adsorption of cationic species with the adsorbed Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> ions. However, Cl<sup>-</sup> ions are involved in specific irreversible chemisorption with metal surface shifting  $\phi_n$  to more positive potentials, leaving the metal surface negatively charged. Thus the metal surface saturated with Cl<sup>-</sup> ions is negatively charged which strongly interact with the cationic species. On the other hand SO<sub>4</sub><sup>2-</sup> ions are only weakly adsorbed and lead to slightly lower adsorption of studied inhibitors.

## 7.4 CONCLUSIONS

The results and discussion arrived based on the investigations of weight loss and electrochemical studies are as follows

- Inhibition efficiency increases and corrosion rate decreases with increasing concentration of the studied inhibitors.
- The inhibition efficiency of the studied inhibitors follow the order  $\text{HCl} > \text{H}_2\text{SO}_4$  by weight loss and electrochemical methods.
- Polarization studies showed that all the studied inhibitors behaved as mixed type but predominantly act as anodic.



## 7.5 REFERENCES

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