INTRODUCTION

Iron and its alloys are extensively used in many engineering applications in various environments especially in inorganic and organic acid environments because of their excellent combination of properties. Concentrated mineral acids are used extensively in picking, cleaning, descaling and oil well acidiying of metallic materials cause corrosion damage to metals. It has been speculated that organic inhibitors are more effective with iron and that polar organic compounds containing sulphur and nitrogen are good corrosion inhibitors for the acidic dissolution of metals.

Many organic inhibitors with hetero atoms have been studied. High electron density of the sulphur and nitrogen atoms in these hetero atoms, help the organic molecules to get chemisorbed onto the metal surface. Due to the aggressiveness of hydrochloric acid and sulphuric acid solutions against structural materials, such as carbon steel, the use of corrosion inhibitors are usually required to minimize the corrosion attack.

IMIDAZOLE AS A CORROSION INHIBITOR FOR MILD STEEL IN ACID MEDIUM

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ABSTRACT

The inhibition effect of imidazole on the corrosion of mild steel in acid medium has been studied by mass loss and polarization techniques between 303 K and 333 K. The inhibition efficiency increased with increase in concentration of inhibitor and temperature from 303 K to 318 K for both acids. But higher temperature at 333 K the inhibition efficiency decreased. The corrosion rate increases with increase in temperature and decreases with increase in concentration of inhibitor compare to blank. The adsorption of this compound on the mild steel surface has been found to obey Temkin's adsorption isotherm. Potentiostatic polarization results reveal that imidazole is a mixed type inhibitor. The values of activation energy and free energy of adsorption were also calculated.

Keywords: Mild steel, sulphuric acid, hydrochloric acid, corrosion inhibitor, Temkin's adsorption, isotherm, potentiostatic polarization and imidazole.

EXPERIMENTAL

Mass loss measurements

Mild steel specimens were cut to size of 5 cm x 1 cm from the mild steel sheets having the following percentage composition: Fe = 99.686, Ni = 0.013, Mo = 0.015, Cr = 0.043, S = 0.014, P = 0.009, Si = 0.007, Mn = 0.196, C = 0.017. Mass loss measurements were performed as per ASTM method described previously. Mass loss measurements were carried out in 1 N sulphuric acid and 1 N hydrochloric acid with imidazole in
the concentration range of 0.1 % to 0.5 % as inhibitor and the temperature between 303 K and 33 K for and immersion period of 4 hours. All the solutions were prepared with AR grade chemicals in double distilled water.

**Potentiostatic Polarization measurement**

Polarization measurements were carried out in a conventional three-electrode cell. Mild steel strips coated with lacquer expect for and exposed area of 1 cm² was used as the working electrode.

### Table - 1: Calculated Corrosion rate, inhibition efficiency (I.E.%) and surface coverage (θ) for imidazol from mass loss studies in 1N Sulphuric Acid and 1N Hydrochloric Acid

| Temperature (K) | Concentration of imidazole (%) | 1N Sulphuric acid Corrosion Rate (mmpy) | Surface Coverage (θ) % | Inhibition Efficiency (%) | 1N Hydrochloric acid Corrosion Rate (mmpy) | Surface Coverage (θ) % | Inhibition Efficiency (%) |
|-----------------|-------------------------------|----------------------------------------|------------------------|---------------------------|---------------------------------------------|------------------------|---------------------------|
| **Blank**       |                               | 63.1552                               | -                      | 15.00                     | -                                           | -                      | -                         |
| 0.1             |                               | 23.9246                               | 0.6211                | 62.11                     | 7.2814                                     | 0.5146                | 51.46                     |
| 0.2             |                               | 19.6895                               | 0.6882                | 68.82                     | 5.7954                                     | 0.6140                | 61.40                     |
| 0.3             |                               | 16.4203                               | 0.7400                | 74.00                     | 4.7552                                     | 0.6833                | 68.33                     |
| 0.4             |                               | 15.2315                               | 0.7588                | 75.88                     | 4.3837                                     | 0.7080                | 70.80                     |
| 0.5             |                               | 14.9343                               | 0.7635                | 76.35                     | 0.7626                                     | 0.7626                | 76.26                     |
| **Blank**       |                               | 455.5348                              | -                      | 371.6526                  | -                                           | -                      | -                         |
| 0.1             |                               | 122.239                               | 0.7317                | 73.17                     | 17.7577                                    | 0.9623                | 95.23                     |
| 0.2             |                               | 104.0203                              | 0.7716                | 77.16                     | 13.0768                                    | 0.9647                | 96.47                     |
| 0.3             |                               | 73.7058                               | 0.8381                | 83.81                     | 12.9282                                    | 0.9651                | 96.51                     |
| 0.4             |                               | 70.8081                               | 0.8445                | 84.45                     | 12.7796                                    | 0.9657                | 96.57                     |
| 0.5             |                               | 68.1333                               | 0.8504                | 85.04                     | 12.3338                                    | 0.9668                | 96.68                     |
| **Blank**       |                               | 634.3012                              | -                      | 507.92                    | -                                           | -                      | -                         |
| 0.1             |                               | 363.7740                              | 0.4264                | 42.64                     | 60.6290                                    | 0.8806                | 88.06                     |
| 0.2             |                               | 347.6508                              | 0.4480                | 44.80                     | 55.5022                                    | 0.8907                | 89.07                     |
| 0.3             |                               | 317.5592                              | 0.4943                | 49.43                     | 51.1185                                    | 0.8993                | 89.93                     |
| 0.4             |                               | 312.5068                              | 0.5073                | 50.73                     | 38.2646                                    | 0.9247                | 92.47                     |
| 0.5             |                               | 309.7577                              | 0.5116                | 51.16                     | 32.9150                                    | 0.9352                | 93.52                     |

**Fig. - 1:** Temkin’s adsorption isotherm for corrosion behaviour of mild steel in 1N sulphuric acid with imidazole
The saturated calomel electrode and the platinum foil were used as reference and counter electrodes respectively. The potentiostatic was carried out using BAS – 100 A model instruments.

**RESULTS AND DISCUSSION**

**Mass loss Studies**

Table -1 shows the value of inhibition efficiency [IE%] surface coverage (q) and corrosion Rate obtained at different concentration of the inhibitors in 1 N sulphuric acid and 1 N hydrochloric acid solution for an immersion period of 4 hours. From the mass value, the inhibition efficiency [IE%] and surface coverage (q) were calculated using the following equation12, 22.

\[
IE\% = \frac{W_u - W_i}{W_u} \times 100 \quad (1)
\]

\[
q = \frac{W_u - W_i}{W_u} \quad (2)
\]

Where \( W_u \) and \( W_i \) are the corrosion rates for mild steel in the absence and presence of inhibitor respectively at the same temperature.

It is clear that the addition of inhibitor to the acid has reduced the corrosion rate. The inhibition efficiency is increased with increase in the concentration of inhibitor and increased with temperature from 303 K to 318 K and then decreased. The values of the corrosion rate and inhibition efficiency of the inhibitor are known to depend on the molecular structure of the inhibitor. The maximum efficiency of imidazole was found to be 85.04% in 1N sulphuric acid and 96.68% in 1 N hydrochloric acid at 0.5% inhibitor concentration at 318 K.

**Thermodynamic / Kinetic Consideration**

Table -2 shows that the calculated values of activation (\( E_a \)) and free energy of absorption (\( G_{ads} \)) for mild steel corrosion in 1 N sulphuric acid and 1 N hydrochloric acid with and without inhibitor. Energy of activation (\( E_a \)) was calculated from Arrhenius equation 23-25.

\[
\log \frac{P_2}{P_1} = \frac{E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]
\]

Where \( P_1 \) and \( P_2 \) are the corrosion rates at temperatures \( T_1 \) and \( T_2 \) respectively. \( E_a \) values for the corrosion of mild steel in 1 N sulphuric acid at temperatures of 303 K, 318K and 333K are 105.542 KJ/Mole, 19,434 and 64.519/mole.
Fig. - 2: Temkin's adsorption isotherm for corrosion behaviour of mild steel in 1N hydrochloric acid with imidazole

Fig. - 3: Typical potentiostatic curves for mild steel in 1N sulphuric acid with imidazole

Fig. - 4: Typical potentiostatic curves for mild steel in 1N hydrochloric acid with imidazole
respectively. And the Ea values for the corrosion of mild steel in 1 N hydrochloric acid at temperatures of 3.3 K, 318 K and 333 K are 171.415 KJ/mole and 98.509 KJ/mole respectively.

In acid containing the inhibitor, the Ea values are found to be lower than that in the uninhibited system at 303 K and 33 K only. At 318 K the Ea values are found to be higher than that in the uninhibited system. The higher values of Ea indicate physical adsorption of the inhibitor on metal surface.

The free of adsorption ($\Delta G_{ads}$) at different temperature was calculated from the following equation:

$$\Delta G_{ads} = -RT \ln (55.5 \text{ K})$$

Where K is given by

$$K = \frac{\theta}{C(1-\theta)}$$

Where $\theta$ is surface coverage on the metal surface $C$ is concentration of inhibitor in mole/lit and K is equilibrium constant.

The negative values of ($\Delta G_{ads}$) indicated the spontaneous adsorption of inhibitor. This is usually characteristic of strong interaction with the metal surface. It is found that the $\Delta G_{ads}$ values are more positive than $-40$ KJ/mole$^{-1}$ indicating that inhibitor is physically adsorbed on the metal surface.

**Adsorption isotherms**

The plot of surface coverage ($\theta$) obtained by mass loss method versus log C at different concentration of the inhibitors shows a straight line indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Timken’s adsorption. This also points out that the corrosion inhibition by imidazole compound is a result of its adsorption on the metal surface. Fig. 1 and 2 shows the Timken’s adsorption plots for imidazole.

**Potentiostatic Polarization studies**

The Polarization behaviors of mild steel functioning as cathode as well as anode in the test solutions is shown in Fig. 3 and 4 for IN sulphuric acid and 1N hydrochloric acid at room temperature. The electrochemical data obtained are shown in Table -3. It is evident that imidazole bring about considerable polarization of cathode as well as anode. It was therefore inferred that the inhibitive action is of a mixed type. The cathodes and anodic Tafel slopes increase with increasing inhibitor concentration. The increase predominant in the case of the former Indicating that the cathodes inhibition is dominating through the inhibitive action is of mixed nature.

The corrosion parameters deduced from Tafel polarization such as corrosion current $I_{corr}$, Corrosion potential $E_{corr}$, Tafel constant $b_a$ and $b_c$ and inhibition efficiency are given in Table III The $I_{corr}$ values decreased with increasing concentration of the inhibitor. The inhibition efficiencies were determined from the values of corrosion current.

**Conclusion**

The following conclusion were made from the studies:

1) Corrosion rates of mild steel 1N sulphuric acid greater than 1N hydrochloric acid at all temperature.
2) Corrosion rates of mild steel in sulphuric acid and hydrochloric acid decreased with

| Concentration inhibitor (%) | $E_{corr}$ Vs SCE(mv) | $I_{corr}$ μA/cm² | Tafel Constant mv/decade $b_a$ | $-b_c$ | 1N Sulphuric acid | Concentration inhibitor (%) | $E_{corr}$ Vs SCE(mv) | $I_{corr}$ μA/cm² | Tafel Constant mv/decade $b_a$ | $-b_c$ | 1N Hydrochloric acid |
|-----------------------------|----------------------|-------------------|-------------------------------|--------|------------------|-----------------------------|----------------------|-------------------|-------------------------------|--------|------------------|
| Blank                       | -500                 | 360               | 45                            | 65     | -               | -495                        | 110                  | 60                | 80                            | -      | -               |
| 0.1                         | -500                 | 300               | 25                            | 30     | 16.66           | -505                        | 95                   | 45                | 30                            | 13.63  | 110              |
| 0.2                         | -495                 | 250               | 30                            | 35     | 30.55           | -515                        | 90                   | 50                | 65                            | 18.18  | 95               |
| 0.3                         | -495                 | 220               | 30                            | 45     | 38.88           | -525                        | 80                   | 90                | 55                            | 27.27  | 95               |
| 0.4                         | -490                 | 180               | 20                            | 30     | 50.00           | -510                        | 70                   | 55                | 50                            | 36.36  | 90               |
| 0.5                         | -505                 | 150               | 20                            | 20     | 58.33           | -515                        | 50                   | 55                | 45                            | 54.54  | 50               |
increasing concentration of imidazole.

3) The inhibition efficiency increased with respect to the concentration of imidazole as it is assumed that the inhibition efficiency is equal to surface coverage.

4) The inhibition efficiency of imidazole in sulphuric acid and hydrochloric acid increased with rise in temperature up to 318 K and then decreased.

5) The maximum inhibition efficiency is found to be 85.04% and 96.68% at 318K for imidazole in 1N sulphuric acid and 1N hydrochloric.

6) The adsorption of imidazole on mild steel surface form the acid solution follows Temken's adsorption isotherm.

7) The low and negative value of $\Delta G_{ads}$ indicated that the imidazole is physically adsorbed and spontaneous adsorption of inhibitor on the surface of mild steel.

8) It is found that the imidazole acting ad mixed type inhibitor.

9) Ea values indicated physical adsorption of the inhibitor on metal surface.

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