

# Effect of Schiff Base Ligands as Corrosion Inhibitors on Mild Steel

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## ABSTRACT

Corrosion is recognized as a major problem in today's manufacturing industries where every industry pays for the cost of corrosion and pays for its control. If we consider mild steel which is extensively used in industries gets corroded when exposed to different industrial corrosive environments. Therefore, this experiment deals with the effort to control the rate of corrosion and increase the stability of the material. Mild steel which is being used is dissolved in 0.1M H<sub>2</sub>SO<sub>4</sub> and corrosion inhibitors can be used to restrain the corrosive attack of acids on the structure. Using organic corrosion inhibitors having hetero atoms in the organic molecule such as nitrogen, oxygen and sulphur are acting as donor atoms. Newly synthesized organic corrosion inhibitors viz., IM1 to IM4 in 0.1M H<sub>2</sub>SO<sub>4</sub>. This helped us to understand acid and inhibitors concentration, immersion time and temperature on dissolution rate and polarization potential have been studied. The mild steel follows adsorption of inhibitors molecules which is been proved through the study of Arrhenius adsorption isotherm.

**Keywords:** inhibitors; polarization; Arrhenius adsorption isotherm;

## I. INTRODUCTION

This experiment deals with the dissolution study of mild steel in 0.1M H<sub>2</sub>SO<sub>4</sub>. It is significant practice since the acid is highly corrosive and extensively used in various industrial operations<sup>1</sup>. The usage of corrosion inhibitors is essential so that it restrains the corrosive attack of acids on metallic materials<sup>2</sup>. Organic compounds containing nitrogen, sulphur and oxygen has been found to function as very effective corrosion inhibitors. The effectiveness of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pairs present, the  $\pi$ -electron character of free electron and the electron density around the nitrogen atoms<sup>3</sup>. This has prompted us to study the new inhibitors IM<sub>1</sub> to IM<sub>4</sub> in 0.1M H<sub>2</sub>SO<sub>4</sub> medium. The effect of acid concentration, immersion time and temperature on dissolution rate and polarization studies has been explored. The

inhibitors action on the mild steel follows absorption of inhibitors molecule which has been proved through the study of Arrhenius adsorption isotherm. It could be obtained from the current potential plots and corrosion rates from Tafel extrapolation method. The corrosion rates obtained from cathodic and anodic polarization techniques are compared to get useful information about the corrosion test in presence of inhibitors tools for mild steel. The thermodynamics parameters were also deduced from the resulting adsorption isotherms and surface coverage values of inhibitors. In view of the above facts we thought of discussing the effects of corrosion inhibitors on mild steel for anodic and chemical dissolution.

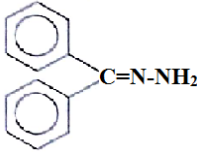
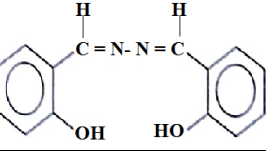
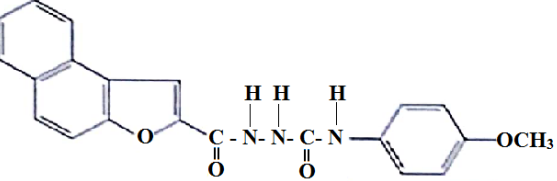
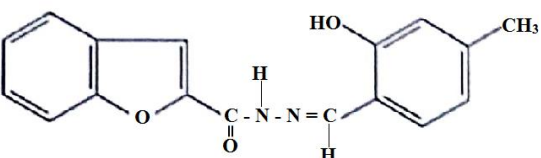
## II. EXPERIMENTAL

### Material and methods

All chemical and reagents were used in this projects were of AR-grade. Further solvents, reagents and

chemicals were purified. The following corrosion inhibitors were used in this paper.

**Table 1**

Inhibitor code	Name of the corrosion inhibitor	Structure
IM <sub>1</sub>	1-(Diphenyl methylene) hydrazine	
IM <sub>2</sub>	2-Hydroxybenzaldehyde[(1E)-(2-hydroxyphenyl)methylene] hydrazone	
IM <sub>3</sub>	N-(4-methoxyphenyl)-2-(naphtha[2,1-b] furan -2-yl-carbonyl)hydrazine carbothioamide	
IM <sub>4</sub>	N'[(1E)-(2-hydroxy- 4-methylphenyl)methylene]-1-benzofuran - 2-carbohydrazide	

#### Preparation of the Electrode Surface:

Mild steel having a surface area of 0.985cm<sup>2</sup> were fixed in a Tygon tubing exposing only the required surface. The metal plates were cleaned mechanically and also emery paper for the removal of organic deposits like grease oil which can be removed by washing with ethanol and orthophosphoric acid. The metal plates were dipped in 0.1M H<sub>2</sub>SO<sub>4</sub> or HCL solution, stirred without and with different concentration of inhibitors for the desired interval of time (1 to 6hrs).

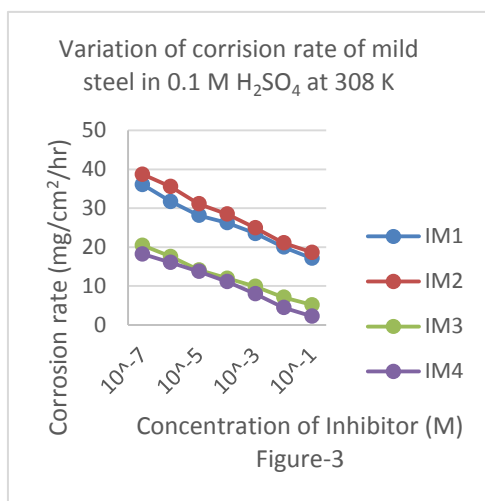
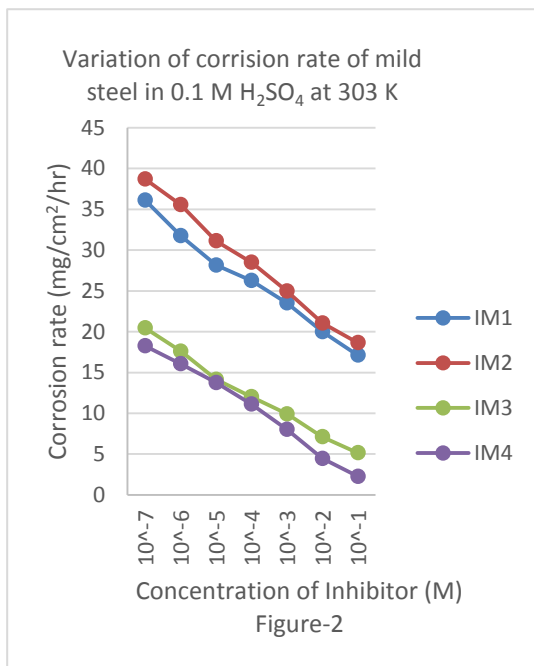
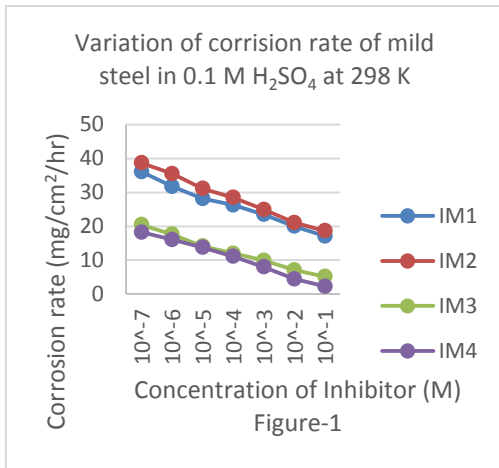
#### Preparation of corrosive medium:

Analytical graded Sulphuric or Hydrochloric acids used for each anodic or chemical dissolution studies was distilled using 1:1 acid-tri-pe water proportion. Distilled was subjected to anodic pre-electrolysis in a cell with platinum electrodes for 12 hours at current density greater than that used in dissolution studies.

### III. RESULTS AND DISCUSSION

#### Dissolution Rates:

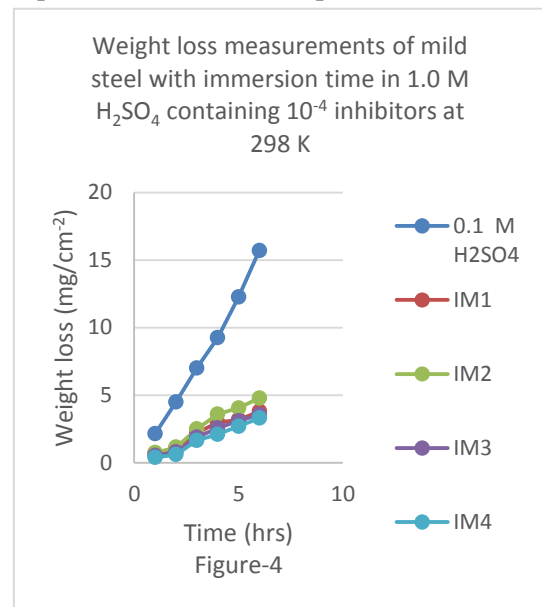
The mild steel surface was exposed to 0.1M H<sub>2</sub>SO<sub>4</sub> under stirred and unstirred conditions in the temperature range of 298-308 K for about 1 to 6 hrs with and without inhibitors at various concentrations (10<sup>-7</sup> M to 10<sup>-1</sup> M). The dissolution rates (mg/cm<sup>2</sup>/hr) of mild steel plates were calculated in corrosive medium spectrophotometrically. The inhibitory effect of inhibitors on the significant dissolution rate of the mild steel was observed. Decrease in the corrosion rate of the mild steel was observed as change in the concentration of inhibitors. The decrease in rate of corrosion was indicated in the graphs. The graph were plotted against "concentration of inhibitors (M) Vs Corrosion rate (mg/cm<sup>2</sup>/hr)" as shown in Figures-1, 2, 3.



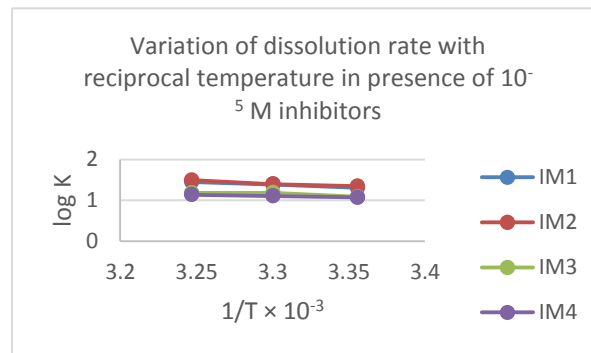
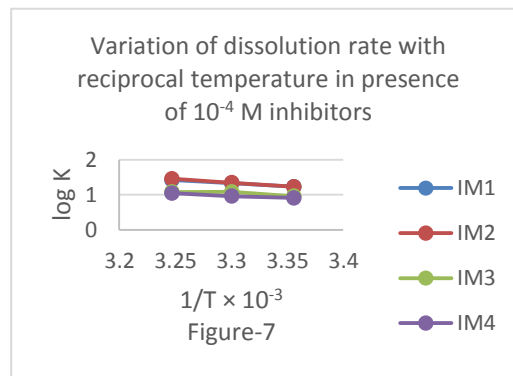
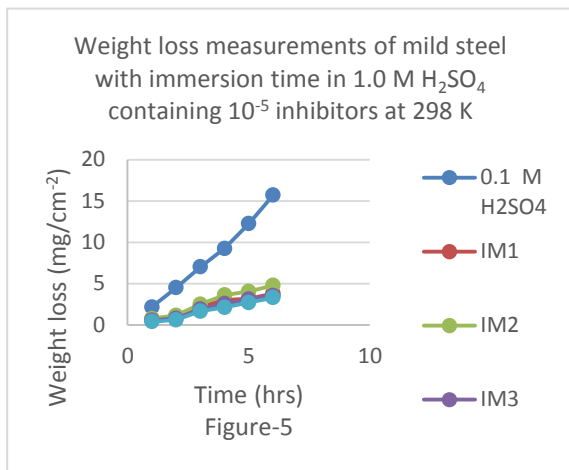
Based on the experimental data clearly reveals under stirred aerated conditions in 0.1M H<sub>2</sub>SO<sub>4</sub> to study the effects of stirring rates on the dissolution of mild steel. The dissolution rates increased with increase in the rate of stirring till to reach optimum stirring rate. Above optimum stirring rate, the dissolution rate of mild steel was independent.

#### Effects of Immersion time:

Mild steel surface was immersed at different intervals of time in 0.1M H<sub>2</sub>SO<sub>4</sub> with different concentrations (10<sup>-7</sup>- 10<sup>-1</sup> M) of inhibitors at 298K. Graphs has been plotted "Time Vs Weight loss" Figs- 4, 5 shows the effects of immersion time on the weight loss of mild steel in 0.1M H<sub>2</sub>SO<sub>4</sub> with (10<sup>-4</sup>- 10<sup>-5</sup> M) inhibitors at room temperature. Inference from the graph is that the mild steel dissolved with steady rate and weight loss was a linear as a function of immersion time. It was observed in the both Figures represents the absence of the insoluble film of corrosion product deposited on the surface. The inhibitor efficiency was calculated and it was found to be independent of immersion period.



#### Effects of Stirring:



### Effects of Temperature:

To study the effects of temperature on the corrosion rate of mild steel in 0.1M H<sub>2</sub>SO<sub>4</sub> contains 10<sup>-4</sup> M - 10<sup>-5</sup> M of inhibitors in the temperature range 298 – 308 K. As increasing in the rate of corrosion by increasing the temperature with or without corrosion inhibitors. However, the inhibitor efficiency was decreased with increase in temperature due to the decomposition of organic inhibitor so the rate of corrosion inhibition is depending on temperature.

The graph has been plotted (log k) Vs 1/T (Figure 6 and 7). These plots clearly reveals the activation energies of the dissolution process in presence of 10<sup>-4</sup> M - 10<sup>-5</sup> M concentration of inhibitors.

The activation energy of different corrosive inhibitors values were tabulated in Table-1. The activation energy of different corrosion inhibitors values are different for different organic molecule. The thermodynamic parameters are obtained at 303K but the entropy value indicates for different corrosion inhibitors reduces the dissolution of the mild steel.

**Table 1.** Thermodynamics parameters at 303K in presence of 10<sup>-3</sup> M inhibitors

Thermodynamics parameters	IM <sub>1</sub>	IM <sub>2</sub>	IM <sub>3</sub>	IM <sub>4</sub>
E <sub>a</sub> (KJ mol <sup>-1</sup> )	070.417	082.89	047.100	027.943
- ΔG <sup>o</sup> <sub>a</sub> (KJ mol <sup>-1</sup> )	045.309	046.295	046.800	022.655
ΔH <sup>o</sup> <sub>a</sub> (KJ mol <sup>-1</sup> )	045.355	046.342	046.847	022.678
ΔS <sup>o</sup> <sub>a</sub> (KJ mol <sup>-1</sup> )	152.190	155.510	157.200	076.100

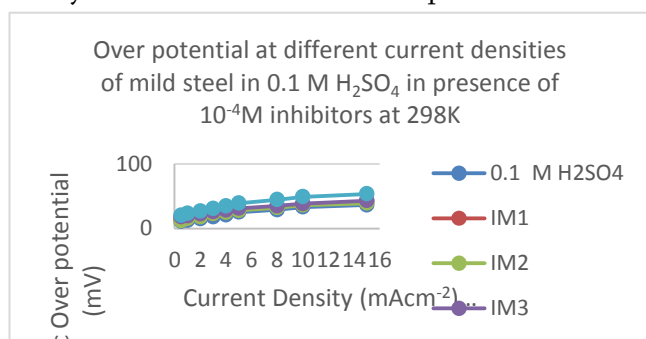
### Corrosion Potential:

In the presence of different concentration corrosion inhibitors the mild steel is immersed and corrosion potential was studied. In absence of corrosion inhibitor the corrosion potential is increased with

increase in immersion time to a certain extent and remains constant. The same trend is observed in variation of corrosion potential in presence of inhibitors. As depicted in Figure 2 and 3.

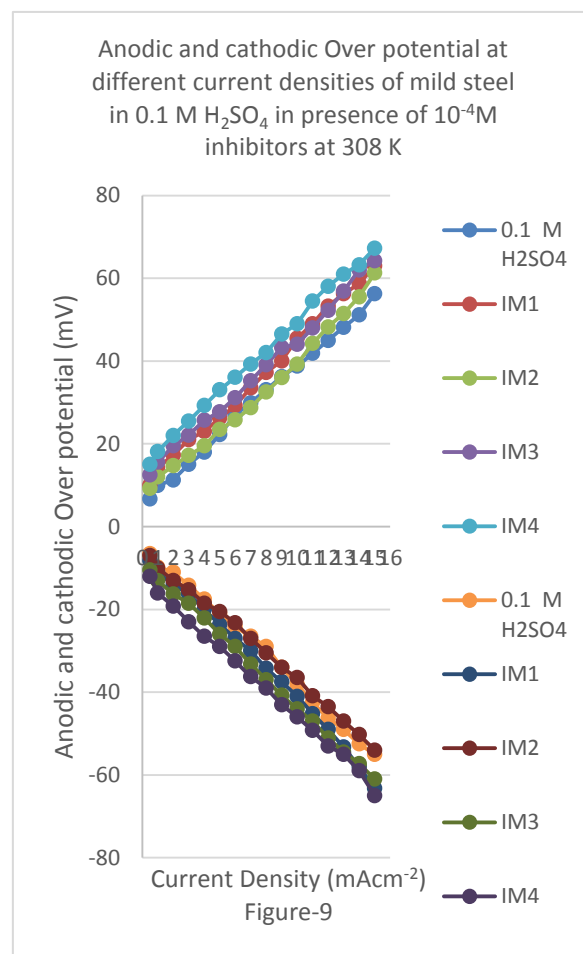
### Polarization measurements:

Mild steel surface was studied under anodic polarization galvanostatically in stirred 0.1M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentration of inhibitors, current densities is maintained between 0.5 and 15mA/cm<sup>2</sup> at 303K. During anodic polarization at each current density, the over potential drifted slightly with time and finally attained a steady value on the surface of the mild steel at all current densities, the anodic over potential increased with time and reached a steady state value in 0.1M H<sub>2</sub>SO<sub>4</sub> as summarized. The same trend was observed in the variation of over potential in presence of different concentration (10<sup>-7</sup> - 10<sup>-1</sup>M) of inhibitors. The value of initial and final over potential were always higher in the presence of inhibitors compared to that of pure acid. Figure 8 represents the variation in over potential with current density in 0.1M H<sub>2</sub>SO<sub>4</sub> at room temperature.



The steady state over potential values were used to construct Tafel plots with and without corrosive inhibitors. Anodic Tafel lines shifted to higher potential region on the surface of metal. The anodic Tafel slope of 40 ± 5mV obtained in 0.1M H<sub>2</sub>SO<sub>4</sub> increased with increasing concentration of inhibitory action of inhibitors. The value of Tafel slopes obtained in presence of inhibitor on the surface of the metal shown in Figure 9. The same trend was observed in the case of cathodic Tafel slope as shown in Figure 9

and this depicts both the anodic and cathodic Tafel slope.



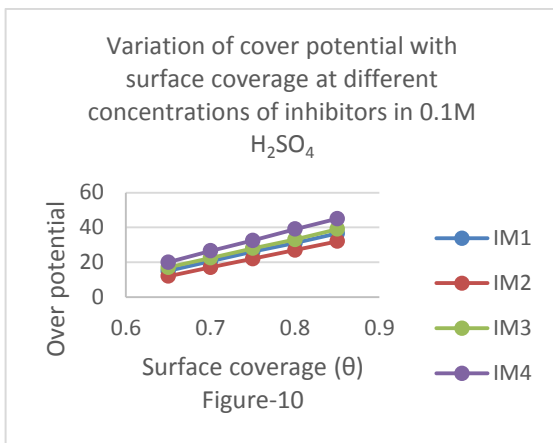
The %P obtained from polarization technique values are aggregable with weight loss method. The surface coverage values obtained from weight loss measurements and polarization technique values and variation in over potential at different concentration in 0.1M H<sub>2</sub>SO<sub>4</sub> is shown in Figure 10.

**Table 2**

Inhibitors	Corrosion current ( <i>i</i> <sub>corr</sub> ) mA/cm <sup>2</sup>	Anodic Tafel slope (β <sub>a</sub> ) mV/decade	Inhibitor efficiency %P
0.1 M H <sub>2</sub> SO <sub>4</sub>	0.35	35.2	-
IM <sub>1</sub>	0.29	41.1	82.00
IM <sub>2</sub>	0.10	39.25	80.24

IM <sub>3</sub>	0.62	98.0	87.00
IM <sub>4</sub>	0.85	40.0	91.02

$$\text{Surface coverage } (\theta) = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}}$$



The percentage protection from the polarization data were evaluated by using the Fisher's equation as follows,

$$\%P = \frac{i - i^*}{i} \times 100$$

Where *i* and *i*' are corrosion current with and without corrosive inhibitors respectively. The %P was calculated using Fisher equation and same values were tabulated in Table- 2.

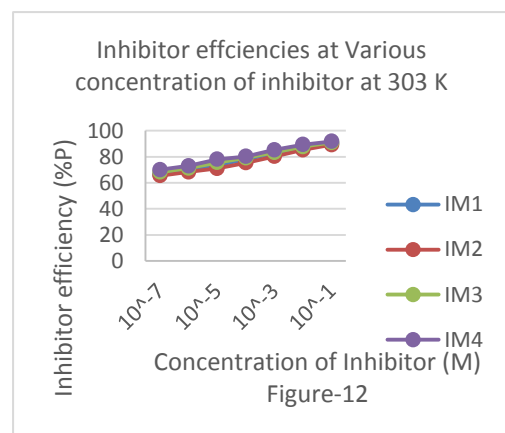
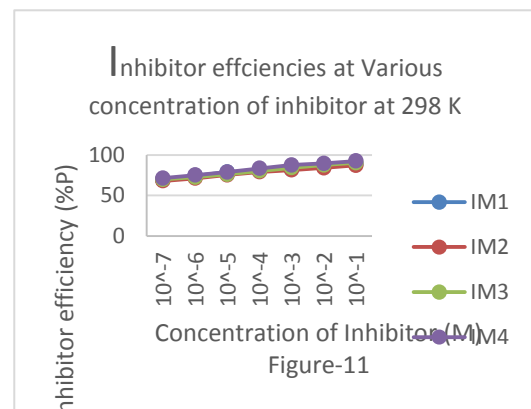
Table-2 Values of Corrosion current (*i*<sub>corr</sub>), Tafel slope (*β*<sub>a</sub>) and %P of mild steel stirred condition.

The weight loss of mild steel in 0.1M H<sub>2</sub>SO<sub>4</sub> and in the presence of the different inhibitors (IM<sub>1</sub>- IM<sub>4</sub>) was determined by maintaining the time duration for about 1 to 6 hrs of immersion. The value of inhibitors efficiency (I.E), corrosion rate and surface coverage (*θ*) were calculated from the weight losses of the specimen with and without corrosive inhibitor using the following equations.

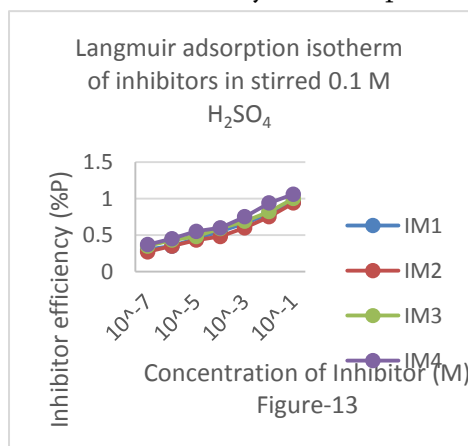
$$\text{I.E} = \frac{\text{Weight loss without inhibitors} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \times 100$$

$$\text{Corrosion rate} = \frac{534 \times \text{Weight loss in mg}}{\text{Density} \times \text{Area in sq.inch} \times \text{Time in hours}}$$

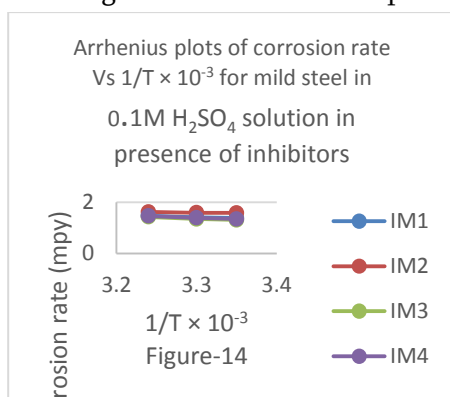
Figure 11 and Figure 12 show the IE for different concentrations of the inhibitors (10<sup>-7</sup>M- 10<sup>-1</sup> M) in 0.1M H<sub>2</sub>SO<sub>4</sub>. It is evident from this figure that all the compounds inhibit the corrosion of mild steel even at very low concentrations. The very high IE of these compounds is understandable from the electron donating properties of different nitrogen atoms present in the molecules. From the molecular structure of the inhibitors it is clear that an extensively delocalized orbit covers all the molecular atoms and the orbit is filled up with a number of *π*-electrons, they being contributed by different anchoring atoms of the molecule. It is apparent from the molecular structure that these molecules are able to absorb on the metal surface through nitrogen, imine groups and aromatic rings<sup>4,5</sup>.



The degree of surface coverage ( $\theta$ ) for the different concentrations of the inhibitors evaluated from weight loss measurement. Inhibitor efficiency is increased as increase in inhibitor concentration. The same indicated in Figure 13. The Langmuir isotherm was tested by plotting  $c/\theta$  Vs  $C$  for all compounds (Figure 13). A straight line obtained in all the cases providing the fact these compounds adsorbed on the mild steel surface obeys the Langmuir adsorption isotherm. This is substantiated by earlier report<sup>6</sup>.



At different temperature in the range of 298K - 308K with and without corrosive inhibitors (IM<sub>1</sub> to IM<sub>4</sub>) at different concentration (10<sup>-7</sup>M to 10<sup>-1</sup>M). The corresponding results are shown in Figure 14 and 15, clearly indicates the rate of corrosion increases with decrease in inhibitor efficiency with increase in temperature. The decrease in IE values by increasing the temperature this may be due to desorption of the inhibitors from the metal surface and thus exposing the metal surface for fresh attack by acid<sup>7</sup>. This observation is agreeable with earlier report.



Values of  $E_a$  and  $\Delta G^{\circ}_a$  are given in Table- 1. The less negative values of  $\Delta G^{\circ}_a$  with increase in temperature indicate physical absorption of the inhibitors on the metal surface<sup>8</sup>. The increase in  $E_a$  values for the inhibited solution in comparison with uninhibited solution may be due to the presence of reactive centres on the inhibitors that can block the active sites for corrosion<sup>9</sup>.

The cathodic and anodic polarization curves of mild steel in 0.1M H<sub>2</sub>SO<sub>4</sub> with and without corrosive inhibitors of 10<sup>-4</sup> concentration (IM<sub>1</sub> to IM<sub>4</sub>) as shown in Figure 14. Similarly, polarization studies were made for other temperature (298K and 303K). Electrochemical parameters such as corrosion current ( $I_{corr}$ ) and %P calculated from Tafel plots are given in Table-2. It is evident from the Tafel slope that it is affected to some extent by the addition of corrosive inhibitors, which shows that the inhibitors are efficient to control the rate of corrosion. Bentisset. al.,<sup>10</sup> have reported such Tafel slopes.

#### IV. CONCLUSION

We have studied the effects of corrosion inhibitors on mild steel for anodic and chemical dissolution. In general the efficiency of corrosive inhibitors of different types of organic molecules IM<sub>1</sub> to IM<sub>4</sub>. It is observed from the weight loss from Tafel slopes and thermodynamic parameters that these inhibitors are effective and efficient inhibitors in the presence of corrosion of mild steel in mineral acidic medium.

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