

## Effect of Azlactones on Corrosion Inhibition of Mild Steel in Acid Medium

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**Abstract:** The inhibition efficiency of azlactones on corrosion behaviour of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> has been evaluated using weight loss, gasometry and atomic absorption spectroscopy techniques which shows increase in inhibition efficiency with increase in concentration. Effect of temperature strongly ensures stronger physisorption of the compounds, which obeys Langmuir adsorption isotherm. The inhibition efficiency has been synergistically enhanced by the addition of halide ions. The kinetic corrosion parameters analysed in terms of impedance data shows a satisfactory agreement with those obtained by potentiodynamic polarisation method.

**Key words:** azlactones, Langmuir adsorption isotherm, synergism

### INTRODUCTION

Most of the well known metal corrosion inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms<sup>[1-5]</sup>. It has been observed that these inhibitors act by adsorption on metal surface which mainly depends on physico-chemical properties of the molecule such as functional group, steric factor, aromaticity, Pi electrons present. The scope of the present study is to determine the inhibition efficiency of synthesized azlactones on mild steel in 1M H<sub>2</sub>SO<sub>4</sub> using electrochemical and non-electrochemical techniques.

**2. Experimental Methods:** The azlactones (Table-1) were synthesised and employed for the evaluation of corrosion inhibition of mild steel.

**2.1 Weight Loss Method:** Mild steel specimens of size 5 cm × 2 cm × 0.5 cm were pickled with concentrated HCl. The plates were washed, dried and polished successively using emery sheets of 1/0, 2/0, 3/0 and 4/0 grades, degreased with trichloroethylene and dried. The initial weight of the polished specimens were taken, and suspended in triplicates using glass hooks in to the corrosive media, 1M H<sub>2</sub>SO<sub>4</sub> taken in 200 ml beaker in the presence and absence of inhibitors. After 3 hours the specimens were removed, washed with running water, dried and reweighed. The inhibition efficiency was calculated using the formula,

$$\text{Efficiency of inhibitor} = \frac{(\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor})}{\text{Weight loss without inhibitor}} \times 100$$

To know the effect of temperature, the above procedure was carried out at different temperatures 30°C, 40°C, 50°C and 60°C.

**2.2 Gasometric Studies:** The polished and degreased mild steel specimens were suspended from the hook of the glass stopper and were introduced in to the cell containing 200 ml of 1M H<sub>2</sub>SO<sub>4</sub> with and without inhibitors. From the volume of hydrogen gas evolved the inhibition efficiency was calculated using the expression,

$$\text{Inhibition efficiency (\%)} = \frac{V_B - V_I}{V_B} \times 100$$

Where,

V<sub>I</sub> and V<sub>B</sub> are Volume of H<sub>2</sub> evolved in the presence and absence of inhibitor.

**2.3 Electrochemical Techniques:** Electrochemical impedance spectroscopy (EIS) and Tafel polarization were carried out in an electrochemical measurement unit (Model 1280 B Solartron, UK).

Electrochemical measurements were carried out in a glass cell with a capacity of 100ml. A platinum electrode and a saturated calomel electrode (SEC) were used as counter electrode and reference electrode respectively. The mild steel electrode embedded in Teflon with an exposed area of 0.785 cm<sup>2</sup> was polished and then placed in the test solution (uninhibited and inhibited solutions of three concentrations) for 10-15 minutes before electrochemical measurement.

**2.3.1 AC-impedance Method:** The EIS measurements were made at corrosion potentials over a frequency

range of 10 kHz to 0.01 Hz with signal amplitude of 10 mV. From the plot of  $Z'$  vs  $Z''$ , charge transfer resistance ( $R_t$ ) and double layer capacitance  $C_{dl}$  were determined and used in the following expression,

$$\text{Inhibition efficiency (\%)} = \frac{R_{t(\text{inh})} - R_{t(\text{blank})}}{R_{t(\text{inh})}} \times 100$$

Where,

$R_{t(\text{inh})}$  and  $R_{t(\text{blank})}$  are charge transfer resistance in the presence and absence of inhibitor.

**2.3.2 Potentiodynamic Polarization Method:** Tafel polarization measurements were made after EIS for a potential range of -200 mV to +200 mV with respect to open circuit potential, at a scan rate of 1 mV/sec. The  $I_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_a$ ,  $b_c$  values were obtained from the Tafel plots using the corresponding “corr view” software and used in the following expression,

$$\text{Inhibition efficiency (\%)} = \frac{I_{\text{corr}(\text{blank})} - I_{\text{corr}(\text{inh})}}{I_{\text{corr}(\text{blank})}} \times 100$$

Where,

$I_{\text{corr}(\text{inh})}$  and  $I_{\text{corr}(\text{blank})}$  are the corrosion current in the presence and absence of inhibitor.

**2.4 Synergistic Effect:** The synergistic effect was studied by the addition of 1mM KI to the mild steel specimen immersed in 1M  $\text{H}_2\text{SO}_4$  containing various concentrations of the inhibitors for a duration of three hours. From the weight loss data the corrosion rate and inhibition efficiency was calculated. The same procedure was repeated by the addition of 1mM KCl, 1mM KBr.

The synergistic parameter (S) was determined using the relationship given by Aramaki and Hackerman to ensure that synergism happens rather than antagonism.

$$S_\theta = \theta_{1+2} / \theta_{1+2}^*$$

Where,

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_{1+2})$$

$\theta_1$  = Surface coverage by halides

$\theta_2$  = Surface coverage by inhibitors

$\theta_{1+2}^*$  = Surface coverage by both halides and inhibitors

**2.6 Atomic Absorption Spectrophotometric Studies:** Atomic absorption spectrophotometer (model GBC 908, Australia) was used for estimating the amount of

dissolved iron in the corroder solution containing various concentrations of the inhibitors in 1M  $\text{H}_2\text{SO}_4$  after exposing the mild steel specimen for three hours. Iron nitrate was used as standard to calibrate the instrument. According to this standard value, the samples were diluted with distilled water and analyzed to detect the amount of dissolved iron. From this amount of dissolved iron the inhibition efficiency was calculated.

$$\text{Inhibition efficiency (\%)} = \frac{B - A}{B} \times 100$$

Where,

A and B – Amount of dissolved iron in the presence and absence of inhibitor

## RESULTS AND DISCUSSION

**3.1 Weight Loss Studies:** The values of inhibition efficiency obtained after three hours of immersion by weight loss method is shown in table 2. The inhibition efficiency increases with concentration and reaches a maximum at 7.5mM.

**Effect of Temperature:** The inhibition efficiency obtained by weight loss measurements at higher temperatures 303-333K in the absence and presence of inhibitor at 7.5mM concentration during 1hr of immersion is given in table 3. It is evident that the efficiency of the inhibitor decreases with increase in temperature.  $E_a$  values have been calculated using Arrhenius plots shown in Fig. 3. Radovici<sup>[6]</sup> distinguished 3 groups of inhibitors according to the temperature effects.

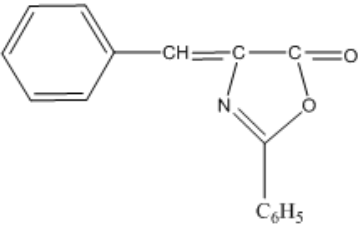
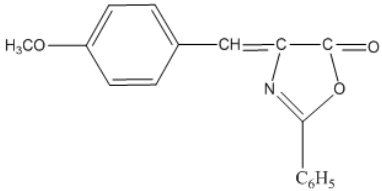
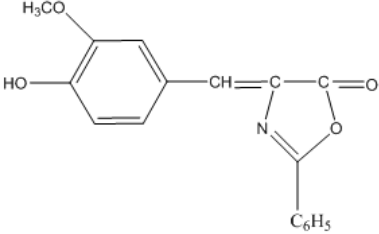
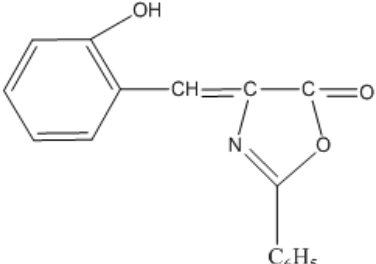
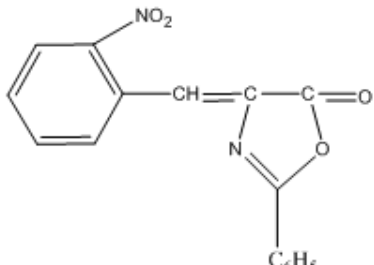
1. The presence of inhibitors leads to decrease of inhibition efficiency with the rise of temperature and an activation energy  $E_a$  greater than that in free acid solution.
2. An efficiency temperature – independent and a constancy of  $E_a$  in the presence and absence of inhibitor.
3. Inhibitors in whose presence the efficiency increases with temperature while the value of  $E_a$  is smaller than that in uninhibited acid.

For the present set of azlactones in 1M  $\text{H}_2\text{SO}_4$ , the inhibition efficiency decreases with temperature and the  $E_a$  values are greater as compared to blank acid value. The data given in the table 3 shows that they are adsorbed by physisorption mechanism.

The adsorption constant  $k_{\text{ads}}$  is related to the standard free energy of adsorption,  $G^\circ$  with the following equation,

$$k = \frac{1}{55.5} \exp \left[ -\frac{\Delta G_{\text{ads}}^\circ}{RT} \right]$$

**Table 1:** Structure of inhibitors

| S.No | Structure of the inhibitors  |
|------|--|
| 1    |  <p>4-benzylidene-2-phenyl oxazol-5-one (AZ1)</p>                         |
| 2    |  <p>4-(4-methoxy benzylidene)-2-phenyl oxazol-5-one (AZ2)</p>            |
| 3    |  <p>4-(4 hydroxy -3methoxy benzylidene)-2-phenyl oxazol-5-one (AZ3)</p> |
| 4    |  <p>4-(2-hydroxy benzylidene)-2-phenyl oxazol-5-one (AZ4)</p>          |
| 5    |  <p>4-(2-Nitro benzylidene)-2-phenyl oxazol-5-one (AZ5)</p>            |

Where,

55.5 is the concentration of water in solution in mol/lit<sup>[7]</sup>.

The calculated  $\Delta G^{\circ}_{ads}$  values (table 3) are negative which ensures the spontaneity of the adsorption process. Generally, values of  $\Delta G^{\circ}_{ads}$  up to -20KJ/mol are consistent with electrostatic interactions (physisorption) while those around -40KJ/mol or higher

are associated with chemisorptions as a result of sharing or transfer of electrons from inhibitor to metal surface to form a co-ordinate bond<sup>[8]</sup>. The values obtained for the present set of compounds are below -20KJ/mol indicating that the adsorption mechanism is only electrostatic.

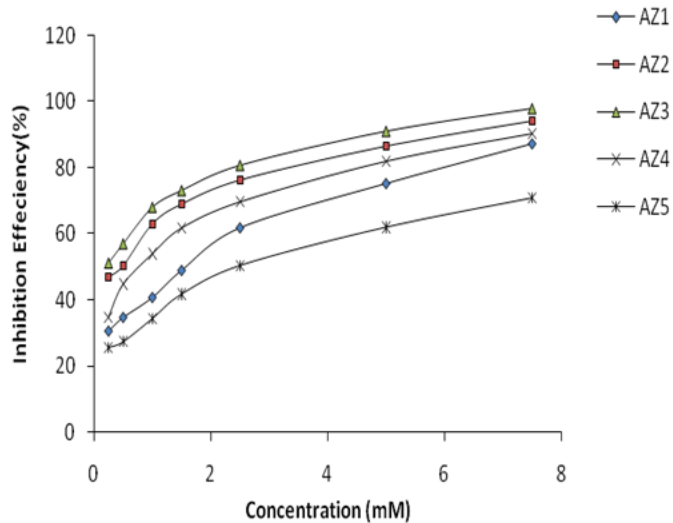
**Mechanism of Adsorption:** It can be proposed that the adsorption of azlactones on the mild steel surface

**Table 2:** Inhibition efficiencies of various concentration of the inhibitors for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> obtained by weight loss method 30+1°C

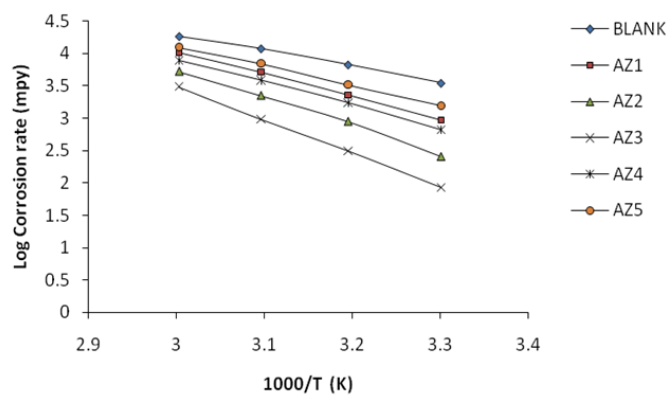
| Conc (mM) | Inhibition Efficiency of inhibitors |       |       |       |       |
|-----------|-------------------------------------|-------|-------|-------|-------|
|           | AZ1                                 | AZ2   | AZ3   | AZ4   | AZ5   |
| Blank     | -                                   | -     | -     | -     | -     |
| 0.25      | 30.47                               | 46.92 | 50.98 | 34.85 | 25.48 |
| 0.5       | 34.61                               | 50.28 | 56.82 | 44.85 | 27.23 |
| 1         | 40.65                               | 62.93 | 67.92 | 54.06 | 34.28 |
| 1.5       | 48.85                               | 68.93 | 73.01 | 61.86 | 41.7  |
| 2.5       | 61.76                               | 76.18 | 80.64 | 69.78 | 50.29 |
| 5         | 75.19                               | 86.4  | 90.98 | 82.07 | 62    |
| 7.5       | 88.23                               | 94.99 | 97.89 | 90.43 | 70.84 |

**Table 3:** Inhibition efficiencies, Activation energies (E<sub>a</sub>) and free energy of adsorption (DG<sup>°</sup><sub>ads</sub>) for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> at 7.5mM concentration of the inhibitors obtained by weight loss measurement at higher temperatures

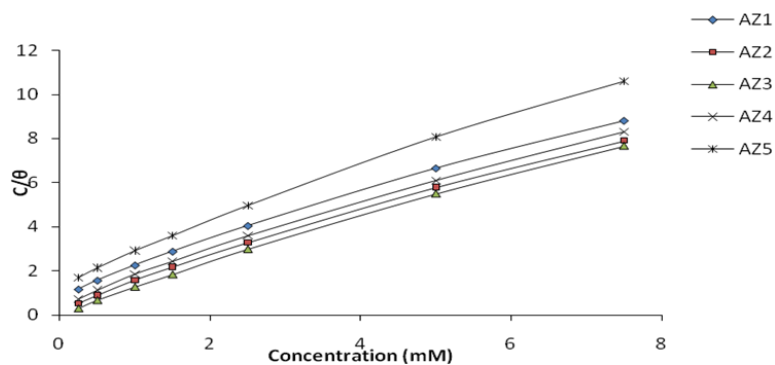
| Name of the inhibitor | Temperature (K) | Weight loss (gms) | Inhibition efficiency (%) | Corrosion rate (mpy) | E <sub>a</sub> (kJ) | (DG <sup>°</sup> <sub>ads</sub> ) |
|-----------------------|-----------------|-------------------|---------------------------|----------------------|---------------------|-----------------------------------|
| BLANK                 | 303             | 0.1560            | -                         | 3491.94              | 42.5                | -                                 |
|                       | 313             | 0.2992            | -                         | 6697.35              |                     | -                                 |
|                       | 323             | 0.5286            | -                         | 11832.28             |                     | -                                 |
|                       | 333             | 0.8136            | -                         | 18211.78             |                     | -                                 |
| AZ1                   | 303             | 0.0416            | 73.33                     | 931.18               | 71.8                | -7.59                             |
|                       | 313             | 0.1012            | 66.18                     | 2265.28              |                     | -6.96                             |
|                       | 323             | 0.2264            | 57.17                     | 5067.78              |                     | -6.15                             |
|                       | 333             | 0.4516            | 44.49                     | 10108.70             |                     | -4.93                             |
| AZ2                   | 303             | 0.0115            | 92.62                     | 257.75               | 104.4               | -11.41                            |
|                       | 313             | 0.0399            | 86.66                     | 895.36               |                     | -10.08                            |
|                       | 323             | 0.1001            | 81.08                     | 2239.24              |                     | -9.28                             |
|                       | 333             | 0.2959            | 63.63                     | 6623.48              |                     | -7.09                             |
| AZ3                   | 303             | 0.0038            | 97.56                     | 85.06                | 105.3               | -14.33                            |
|                       | 313             | 0.0139            | 95.35                     | 312.96               |                     | -13.07                            |
|                       | 323             | 0.0354            | 88.17                     | 792.40               |                     | -10.78                            |
|                       | 333             | 0.1356            | 83.33                     | 3035.29              |                     | -9.99                             |
| AZ4                   | 303             | 0.0354            | 77.30                     | 792.40               | 95.7                | -8.13                             |
|                       | 313             | 0.0976            | 67.38                     | 2184.69              |                     | -7.09                             |
|                       | 323             | 0.2756            | 47.84                     | 6169.09              |                     | -5.14                             |
|                       | 333             | 0.6378            | 21.61                     | 14276.64             |                     | -1.97                             |
| AZ5                   | 303             | 0.0692            | 55.64                     | 1549.89              | 59.5                | -5.61                             |
|                       | 313             | 0.1448            | 51.60                     | 3241.90              |                     | -5.38                             |
|                       | 323             | 0.3112            | 41.13                     | 6965.96              |                     | -4.41                             |
|                       | 333             | 0.6964            | 14.41                     | 15588.26             |                     | -0.61                             |



**Fig. 1:** Plot of inhibition efficiency (%) Vs concentration (mM) for the inhibition of corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub>



**Fig. 2:** Arrhenius plot of corrosion rate of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> Solutions in the absence and presence of inhibitors



**Fig. 3:** Langmuir plot of inhibitors for mild steel in 1M H<sub>2</sub>SO<sub>4</sub>

could occur by electrostatic interaction in three ways

- a) In acidic solution the compounds can exist as protonated species. The probable site of protonation being the N atom of the azlactone ring. These protonated species may adsorb on the cathodic sites of mild steel and decrease the hydrogen evolution.
- b) These compounds are able to adsorb on anodic sites through lone pair of electrons of the nitrogen atom,  $\pi$ -electrons of aromatic ring and C O group and decrease the anodic dissolution of the mild steel.
- c) Combination of the above two<sup>[9]</sup>

**Adsorption Isotherm:** Weight loss data were tested graphically for fitting a suitable isotherm. Plot of  $C/\theta$  Vs  $C$  for all the compounds gave a straight line as shown in Fig.3 proving that these compounds obey Langmuir adsorption isotherm.

**Comparison of Inhibition Efficiency of Synthesized Inhibitors:** The order of inhibition efficiency of the azlactones in 1M  $H_2SO_4$  is  
 $AZ3 > AZ2 > AZ4 > AZ1 > AZ5$

The effectiveness of a compound as corrosion inhibitor depends mainly on the size and active centres of the compound. All the azlactones have almost the same size but they possess different substituent groups. The best performance of AZ3 may be attributed to the presence of two electron releasing groups (-OH &  $OCH_3$ ) which increases the  $\pi$  electron density on the phenyl ring.

AZ2 & AZ4 having either -OH or  $OCH_3$  group show somewhat lower efficiency than AZ3. The nucleophilic character of -  $OCH_3$  group is greater compared to -OH group and hence AZ2 shows higher IE (about 4% more)

The lower inhibition efficiency shown by AZ5 is not only due to the presence of electron withdrawing  $NO_2$  group, but also due to the reduction of the  $NO_2$  group in acid medium in the presence of Fe. The evolved heat of hydrogenation may aid the desorption of the molecule from the steel surface and lowers the efficiency of the compound. Similar result has been reported by Elewady et al for the nitro substituted pyrimidine derivatives<sup>[10]</sup>.

**Gasometric Method:** The corrosion of mild steel and inhibition by the synthesised azlactones were assessed by  $H_2$  gas evolution rate at different concentrations. Table 4 shows the data for Gasometric measurements. These values ensures that the volume of hydrogen gas collected decreased with addition of inhibitor causing the inhibition efficiency to increase with the concentration which agrees well with weight loss measurements.

**3.3 Electrochemical Techniques:** Electrochemical impedance spectroscopy becomes a very important tool in the study of the inhibition of corrosion of metals. This method permits to superimpose a small sinusoidal excitation to an applied potential and then the electrochemical interface metal/solution offers impedance. From the various impedance data, interfaces are described by equivalent circuits involving resistors, capacitors and also inductances<sup>[11]</sup>.

**3.3.1 AC-impedance Method:** The Nyquist plots obtained for mild steel in 1M  $H_2SO_4$  with selected concentrations of the inhibitors is shown in Fig.4. In many cases the impedance diagrams are not perfect semicircle. This can be attributed to the frequency dispersion as a result of roughness and inhomogeneity of the electrode surface<sup>[12]</sup>. The impedance response consisted of characteristic semicircles for the solution shows that the dissolution of mild steel occurs under charge transfer control and the presence of inhibitors does not change the mechanism of acid dissolution. The semicircles are of a capacitive type whose diameter increases with increase in inhibitor concentration.

The Nyquist plots were analysed by fitting the experimental data to a simple equivalent circuit model which includes solution resistance  $R_s$ , double layer capacitance  $C_{dl}$  which is placed in parallel to charge transfer resistance  $R_t$ <sup>[13]</sup>.  $R_t$  values were calculated from the difference in impedance at low and high frequencies. The values of  $R_t$  is a measure of electron transfer across the surface and inversely proportional to the corrosion rate. The double layer capacitance were calculated at the frequency  $f_{max}$  at which the imaginary component of impedance is maximal by the equation,

$$C_{dl} = 1/2\pi f_{max} R_t$$

The values of  $R_t$ ,  $C_{dl}$  and inhibition efficiency(%) for mild steel corrosion in 1M  $H_2SO_4$  are given in table 5. The data indicate that increasing  $R_t$  is associated with a decrease in  $C_{dl}$  and increase in inhibition efficiency.  $R_t$  values increase with increase in concentration indicating an insulated adsorption film formation<sup>[14]</sup>. Further the decrease in  $C_{dl}$  value may be due to the replacement of water molecules at the electrode interface by organic inhibitor of lower dielectric constant through adsorption.

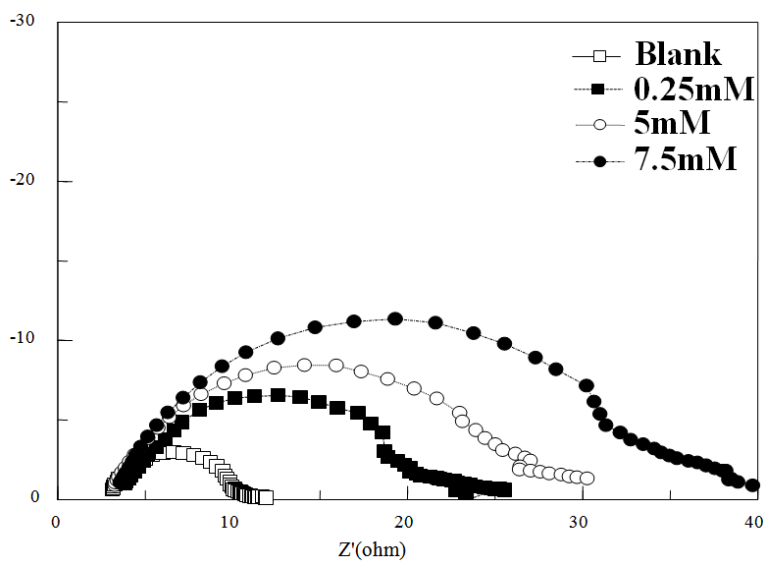
**3.3.2 Potentiodynamic Polarisation Studies:** Fig. 5 presents the anodic and cathodic Tafel curves of mild steel in 1M  $H_2SO_4$ . The values of anodic and cathodic Tafel constants and the corrosion current density are listed in table 6. The anodic and cathodic Tafel lines

**Table 4:** Inhibition efficiencies of various concentration of the inhibitors for the corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> obtained by gasometric method

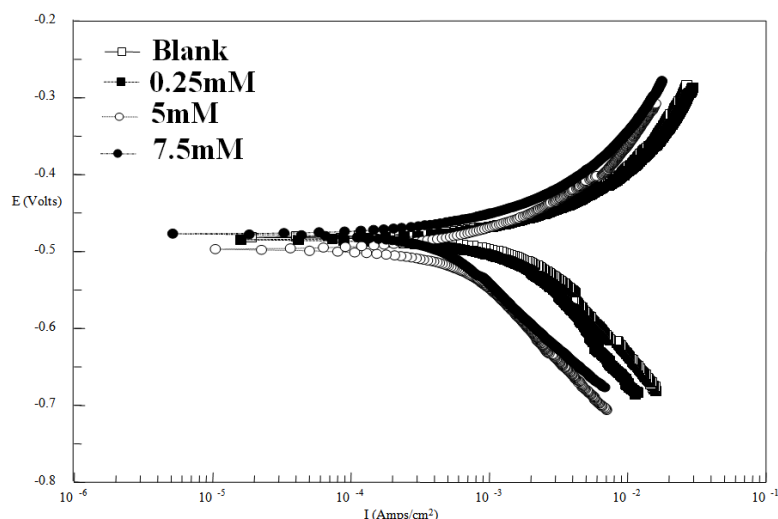
| Conc (mM) | Inhibition Efficiency of inhibitors |       |       |       |       |
|-----------|-------------------------------------|-------|-------|-------|-------|
|           | AZ1                                 | AZ2   | AZ3   | AZ4   | AZ5   |
| Blank     | -                                   | -     | -     | -     | -     |
| 0.25      | 35.36                               | 47.96 | 54.47 | 42.27 | 28.86 |
| 5.0       | 70.73                               | 79.26 | 80.89 | 77.23 | 67.07 |
| 7.5       | 86.17                               | 93.90 | 95.52 | 89.83 | 76.01 |

**Table 5:** AC-impedance parameters for mild steel for selected concentrations of the inhibitors in 1M H<sub>2</sub>SO<sub>4</sub>

| Name of the inhibitor | Inhibitor concentration (mM) | R <sub>p</sub> (ohmcm <sup>2</sup> ) | C <sub>dl</sub> (mF/cm <sup>2</sup> ) | Inhibition efficiency (%) |
|-----------------------|------------------------------|--------------------------------------|---------------------------------------|---------------------------|
| AZ1                   | Blank                        | 7.3287                               | 21.175                                | -                         |
|                       | 0.25                         | 17.428                               | 17.475                                | 57.95                     |
|                       | 5                            | 23.313                               | 17.117                                | 68.56                     |
|                       | 7.5                          | 39.46                                | 14.55                                 | 81.43                     |
| AZ2                   | 0.25                         | 16.394                               | 15.55                                 | 55.29                     |
|                       | 5                            | 55.566                               | 12.67                                 | 86.81                     |
|                       | 7.5                          | 108.12                               | 10.77                                 | 93.22                     |
| AZ3                   | 0.25                         | 10.975                               | 17.36                                 | 33.22                     |
|                       | 5                            | 22.101                               | 9.37                                  | 66.84                     |
|                       | 7.5                          | 130.39                               | 7.91                                  | 94.38                     |
| AZ4                   | 0.25                         | 34.399                               | 15.92                                 | 78.69                     |
|                       | 5                            | 53.644                               | 13.65                                 | 86.34                     |
|                       | 7.5                          | 64.867                               | 7.53                                  | 88.70                     |
| AZ5                   | 0.25                         | 16.071                               | 13.46                                 | 54.39                     |
|                       | 5                            | 23.794                               | 13.26                                 | 69.19                     |
|                       | 7.5                          | 32.37                                | 12.65                                 | 77.35                     |



**Fig 4:** Nyquist diagram for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> for selected Concentrations of the inhibitor AZ1



**Fig. 5:** Polarization curves for mild steel recorded in 1M H<sub>2</sub>SO<sub>4</sub> for selected Concentrations of inhibitor AZ1.

for mild steel in the presence of azlactones are almost parallel upon increasing the concentration. This suggests that the inhibitor act by simple blocking of the mild steel surface and does not change the mechanism of steel dissolution or H<sub>2</sub> evolution<sup>[15]</sup>.

It has been reported that only when the change in E<sub>corr</sub> value is not less than 80mV, a compound can be recognised as an anodic or a cathodic type inhibitor<sup>[16]</sup>. Analysis of E<sub>corr</sub> values (table 6) shows that the largest displacement of the potentials were about 23 in the presence of AZ3 and AZ4. Therefore they act as mixed type inhibitors. The values of ba and bc are both influenced by the presence of inhibitors which suggest that the azlactones are mixed type inhibitors.

The corrosion current densities were estimated by Tafel extrapolation of the Tafel curves to the open circuit potentials. Table 6 shows that the I<sub>corr</sub> values decrease considerably in the presence of inhibitor and that the maximum decrease in I<sub>corr</sub> (64 μAmp cm<sup>-2</sup>) coincides with AZ3 at 7.5 mM concentration indicating it greater inhibition ability.

**3.4 Synergism and its Parameter (S):** As seen from table 2, the inhibition efficiency of AZ1, AZ2, AZ4, AZ5 are comparatively low. So in order to increase the inhibition efficiency halide salts such as (KCl, KBr, KI) were added to the different concentrations of the azlactones. The synergistic effect provided by the addition of 1mM halide ions I<sup>-</sup>, Br<sup>-</sup> and Cl<sup>-</sup> to the solutions containing 1M H<sub>2</sub>SO<sub>4</sub> and the azlactones (AZ1, AZ2, AZ4, AZ5) are presented in table 7.

It can be seen that addition of KI inhibits the corrosion of mild steel to a large extent compared to KCl and KBr at all concentrations of the inhibitors. This can be interpreted according to Fouda *et al*<sup>[17]</sup> who

proposed two types of joint adsorption. They are co-adsorption and competitive adsorption.

In competitive adsorption cation and anion are adsorbed at different sites on the electrode surface and in the case of co-operative adsorption, the anions are chemisorbed on the surface of the electrode and the cations are adsorbed on a layer of the anion in addition to the adsorption on the surface directly.

Azlactones are protonated in acid medium and exist as cations. The halide ions are first chemisorbed on the positively charged iron surface. The inhibitors are then adsorbed by coulombic attraction on the surface. This leads to greater surface coverage and thereby greater inhibition.

**Significance of Synergistic Parameter:** The synergism parameter was calculated using the relationship given by Aramaki and Hackerman

$$S = \theta_{1+2} / \theta'_{1+2}$$

Where,

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta'_{1+2})$$

$\theta_1$  = Surface coverage by halides

$\theta_2$  = Surface coverage by inhibitors

$\theta'_{1+2}$  = Surface coverage by both halides and inhibitors

The significance of synergism parameter S is that a value of S > 1 denotes synergism while a value of S < 1 denotes antagonism.

In the present work, the synergism parameter calculated for the three halide ions Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> have been presented in table 7. All the S values are



**Table 6:** Corrosion parameters for mild steel with selected concentrations of the inhibitors in 1M H<sub>2</sub>SO<sub>4</sub> by potentiodynamic polarization method

| Name of the inhibitor | Inhibitor concentration (mM) | Tafel slopes (mV/dec) |                | E <sub>corr</sub> (mV) | I <sub>corr</sub> (mA/cm <sup>2</sup> ) | Inhibition efficiency (%) |
|-----------------------|------------------------------|-----------------------|----------------|------------------------|---|---------------------------|
|                       |                              | b <sub>a</sub>        | b <sub>c</sub> |                        |   |                           |
| AZ1                   | Blank                        | 98.38                 | 157.63         | -481.5                 | 4310                                    | -                         |
|                       | 0.25                         | 55.07                 | 105.04         | -485                   | 2803.5                                  | 34.95                     |
|                       | 5                            | 40.18                 | 142.53         | -497.4                 | 1285.2                                  | 70.18                     |
|                       | 7.5                          | 55.08                 | 100.58         | -478.1                 | 812.42                                  | 81.15                     |
| AZ2                   | 0.25                         | 45.93                 | 117.4          | -483.9                 | 2785.9                                  | 35.36                     |
|                       | 5                            | 60.59                 | 186.05         | -480.2                 | 2568.8                                  | 40.39                     |
|                       | 7.5                          | 82.51                 | 185.01         | -476.4                 | 290.58                                  | 93.26                     |
| AZ3                   | 0.25                         | 83.09                 | 156.57         | -504.1                 | 3482.3                                  | 19.20                     |
|                       | 5                            | 73.73                 | 152.52         | -495.5                 | 188.42                                  | 95.63                     |
|                       | 7.5                          | 60.71                 | 128.62         | -489.5                 | 64.077                                  | 98.51                     |
| AZ4                   | 0.25                         | 88.7                  | 177.57         | -501.1                 | 2428.7                                  | 43.65                     |
|                       | 5                            | 81.96                 | 136.64         | -499.7                 | 658.27                                  | 84.73                     |
|                       | 7.5                          | 71.09                 | 197.1          | -509.4                 | 700.62                                  | 83.74                     |
| AZ5                   | 0.25                         | 65.06                 | 159.38         | -487.7                 | 2734.3                                  | 36.56                     |
|                       | 5                            | 66.68                 | 169.8          | -483.9                 | 1919.9                                  | 55.45                     |
|                       | 7.5                          | 57.2                  | 126.4          | -482.9                 | 1574                                    | 63.48                     |

**Table 7:** Synergistic effect and Synergistic parameter (S<sub>0</sub>) of 1mM KCl / 1mM KBr / 1mM KI on the inhibition efficiency of Azlactones by weight loss method at 30±1°C

| Name of the inhibitor | Inhibitor conc.(mM) | Inhibition efficiency ( %) and Synergistic parameter ( S <sub>0</sub> ) |                    |             |                    |              |                    |              |                    |
|-----------------------|---------------------|---|--------------------|-------------|--------------------|--------------|--------------------|--------------|--------------------|
|                       |                     | Without Kel, KBr & KI   |                    | With 1mM KI |                    | With 1mM KBr |                    | With 1mM Kel |                    |
|                       |                     | IE(%)   | ( S <sub>0</sub> ) | IE(%)       | ( S <sub>0</sub> ) | IE(%)        | ( S <sub>0</sub> ) | IE(%)        | ( S <sub>0</sub> ) |
| AZ1                   | 0.25                | 28.01   | -                  | 65.26       | 1                  | 57.25        | 1.19               | 53.20        | 1.37               |
|                       | 0.5                 | 35.24   | -                  | 80.41       | 1.02               | 65.20        | 1.32               | 60.95        | 1.48               |
|                       | 1                   | 40.93   | -                  | 83.92       | 1.14               | 70.29        | 1.41               | 67.03        | 1.60               |
|                       | 1.5                 | 51.64   | -                  | 89.90       | 1.48               | 80.32        | 1.74               | 70.12        | 1.45               |
|                       | 2.5                 | 64.22   | -                  | 93.84       | 1.80               | 86.62        | 1.89               | 84.86        | 2.11               |
| AZ2                   | 0.25                | 43.84   | -                  | 83.25       | 1.04               | 65.01        | 1.14               | 52.28        | 1.05               |
|                       | 0.5                 | 51.28   | -                  | 86.22       | 1.09               | 73.84        | 1.32               | 70.48        | 1.48               |
|                       | 1                   | 63.86   | -                  | 90.44       | 1.17               | 88.49        | 2.23               | 87.89        | 2.68               |
|                       | 1.5                 | 67.19   | -                  | 93.05       | 1.46               | 92.88        | 3.27               | 92.40        | 3.86               |
|                       | 2.5                 | 74.92   | -                  | 97.93       | 3.75               | 94.95        | 3.53               | 94.76        | 4.28               |
| AZ4                   | 0.25                | 36.29   | -                  | 80.63       | 1.03               | 55.78        | 1.02               | 46.04        | 1.06               |
|                       | 0.5                 | 47.11   | -                  | 85.73       | 1.15               | 65.53        | 1.09               | 60.68        | 1.21               |
|                       | 1                   | 59.08   | -                  | 89.49       | 1.21               | 74.10        | 1.12               | 59.59        | 1.1                |
|                       | 1.5                 | 63.73   | -                  | 91.62       | 1.34               | 83.19        | 1.53               | 79.18        | 1.56               |
|                       | 2.5                 | 70.09   | -                  | 93.94       | 1.53               | 87.68        | 1.72               | 80.65        | 1.38               |
| AZ5                   | 0.25                | 27.91   | -                  | 77.98       | 1.01               | 51.95        | 1.07               | 35.6         | 1.01               |
|                       | 0.5                 | 30.80   | -                  | 79.97       | 1.07               | 65.56        | 1.43               | 43.87        | 1.10               |
|                       | 1                   | 35.94   | -                  | 82.85       | 1.16               | 77.69        | 2.04               | 62.78        | 1.54               |
|                       | 1.5                 | 45.07   | -                  | 87.85       | 1.39               | 81.55        | 2.11               | 72.36        | 1.78               |
|                       | 2.5                 | 50.13   | -                  | 89.39       | 1.46               | 85.66        | 2.47               | 79.98        | 2.23               |

**Table 8:** Atomic absorption spectroscopic results

| Conc (mM) | AZ1                          |        | AZ2                          |        |
|-----------|------------------------------|--------|------------------------------|--------|
|           | Amount of iron content(mg/l) | IE (%) | Amount of iron content(mg/l) | IE (%) |
| Blank     | 4154.5                       | -      | 4154.5                       | -      |
| 0.25      | 2396.73                      | 42.31  | 1409                         | 66.08  |
| 5.0       | 1299.52                      | 68.72  | 725.4                        | 82.54  |
| 7.5       | 609.04                       | 85.34  | 279.7                        | 93.26  |

greater than unity indicating that the corrosion inhibition by the azlactones (AZ1,AZ2,AZ4,AZ5) has been enhanced by the addition of halide ions and hence it can be concluded that all the halide ions have synergistically influenced the inhibition . Further the S value increases in the order  $Cl^- < Br^- < I^-$  giving highest synergistic influence for  $I^-$  which is in accordance with the findings noted in the literature<sup>[18]</sup>

The synergistic effect of the salts decreases in the order  $KI > KBr > KCl$ . The electronegativity decreases while the atomic radius increases from  $Cl^-$  to  $I^-$ . Therefore ionic radii plays a major role which results in greater surface coverage and adsorption.

**3.5 Atomic Absorption Spectral Studies:** Percentage inhibition efficiency of the inhibitors (AZ1 and AZ2) towards the dissolution of iron was calculated for three different concentrations. The results are given in table 7 which shows that increase in concentration decreases the amount of iron content dissolved resulting in increased inhibition efficiency. The percentage inhibition efficiency obtained by this technique was found to be in good agreement with that obtained from the conventional weight loss method.

**Conclusions:** The condensation products of Schiff bases and hippuric acid (azlactones) possess heteroatoms (N,O-) which makes them effective corrosion inhibitors of mild steel by forming an insoluble protective surface film which suppresses the metal dissolution. From the various techniques, following main conclusions have been drawn from the present study.

The azlactones are found to inhibit the corrosion of mild steel in 1M  $H_2SO_4$  and in the following order of inhibition efficiency.



The inhibition efficiency increases with increase in concentration but decreases with temperature and activation energy ( $E_a$ ) is higher for the inhibited acids than uninhibited acid showing the temperature dependence of inhibition efficiency.

The less negative values of  $\Delta G^{\circ}_{ads}$  ( $< -20KJ$ ) indicates the spontaneous adsorption which is electrostatic interaction

Addition of halide ions leads to pronounced increase in inhibition efficiency in which coulombic attraction prevails

EIS technique shows that an increase in inhibitor concentration is incorporated with an increase in polarization resistance  $R_p$  and decrease in  $C_{dl}$  values owing to the increased thickness of adsorbed layer.

The Tafel slopes obtained from potentiodynamic polarization study indicates that azlactones behave as mixed type inhibitors for mild steel specimens.

## REFERENCES

1. Larabi, L., Y. Harek, O. Benali, S. Ghalem, 2005. Hydrazide derivatives as corrosion inhibitors for mild steel in 1M HCl, progress in organic coatings, 54: 256-262.
2. Chetouani, A., B. Hammouti, T. Benhadda, M. Daoudi, 2005. Inhibitive action of bipyrazolic type organic compounds towards corrosion of pure iron in acidic media, Applied surface science, 249: 375-385.
3. Ashassi-Sorkhabi, H., B. Shaabani, D. Seifzadeh, 2005. Effect of some pyrimidine Schiff bases on the corrosion of mild steel in hydrochloric acid solution, Electrochimica Acta, 50: 3446-3452.
4. Quaraishi, M.A., 2002. Rana Sardar, influence of dithiazolidines on corrosion inhibition for mild steel in sulphuric acid solution, Bulletin of electrochemistry, 18(11): 515-519.
5. Quaraishi, M.A., M.A. Wajid Khan, M. Ajmal, S. Muralidharan, S. Venkatakrisna Iyer, 1966. Influence of substituted benzothiazoles on corrosion of mild steel in acid solution, Journal of Applied Electrochemistry, 26(12): 1253-1258.
6. Radovici, O., 1965. Proceedings of the second European symposium on corrosion inhibitors, Ferrara, 178.
7. Flis, J., T. Zakroczymski, Impedance study of Reinforcing steel in simulated pore solution with tannin, J. Electrochem. Soc., 143(8): 2458-2464.

8. Khamis, E., F. Belluci, R.M. Latanision, E.S.H. El-Ashry, 1991. Triazole Derivatives as corrosion inhibitors for mild steel in hydrochloric acid solution, *corros*, 47: 677-683.
9. Karakus, M., M. Shin, S. Bilgic, 2005. An investigation on the inhibition effects of some new dithiophosphonic acid mono ethers on the corrosion of steel in 1M HCl medium, *Materials chemistry and physics*, 92: 565-571.
10. Elewady, G.Y., 2008. Pyrimidine Derivatives as corrosion inhibitors for carbon –steel in 2M hydrochloric acid solution, *International Journal of Electrochemical Science*, 3: 1149-1161.
11. Ouchrif, A., M. Zegmout, B. Hammouti, S. El-Kdiri and A. Ramdani, 2005. 1,3-Bis(3-hydroxymethyl-5-methyl-1-pyrazole propane as corrosion inhibitor for steel in 0.5M sulphuric acid solution, *App surf sci.*, 252: 339-344.
12. Jeyaprabha, C., S. Sathiyarayanan, G. Venkatachari, 2005. Corrosion inhibition of pure iron in 0.5 M sulphuric acid solutions by ethanolamines, *App surf sci.*, 246(1-3): 108-116.
13. Macdoald, D.D., 1977. *Transient techniques in electrochemistry*, Plenum press, N.Y.
14. Khaled, K.F. and N. Hackerman, 2004. Investigation of the inhibitive effect of ortho-substituted anilines on corrosion of iron in 0.5 M sulphuric acid solutions, *J. mater. Chem. phy.*, 82(3): 949-960.
15. Manahan, S.E., 1966. *Environmental chemistry* 6<sup>th</sup> edn, Lewis Publishers chapter-6.
16. Ashassi-Sorkhabi, H., M.R. Majidi and K. Seyyedi, 2004. Investigation of inhibition effect of some amino acids against steel corrosion in Hcl solution, *J.Appl surf Sci.*, 225(1-4): 176-185.
17. Fouda, A.S., H.A. Mostafa, F. El-Taib, G.Y. Elewady, 2005. Synergistic influence of iodine ions on the inhibitions of corrosion of carbon steel in sulphuric acid by some aliphatic amines, *corros. sci.*, 47(8): 1988-2004.
18. Saratha, C. Marikannu and S. Sivakamasundari, 2002. Corrosion behaviour of mild steel in sulphuric acid -Effect of Halides, *Bull. Electrochem.*, 18: 141-144.