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# Corrosion Inhibition Performance of Azure A on Mild Steel in Sulphuric Acid Medium

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# ABSTRACT

The inhibitive action of azure A (AA) against the corrosion of mild steel (MS) in 0.5 M  $H_2SO_4$  solution was studied by gravimetric and electrochemical techniques. The inhibition efficiency increased with increase in concentration of AA. The adsorption of AA on mild steel surface obeys Langmuir adsorption isotherm. Polarization measurements showed that the studied inhibitor is mixed type with significant reduction of cathodic and anodic current densities. Electrochemical impedance spectroscopy measurements revealed that the charge transfer resistance increases with increase in the concentration of AA. Various thermodynamic and adsorption parameters are evaluated and discussed. The inhibition efficiency of AA synergistically increased by the addition of KI. The relation between inhibition efficiency and molecular structure of AA is discussed by considering quantum chemical parameters.

Keywords: Mild steel, azure A, acid corrosion, EIS, polarization

# INTRODUCTION

Among different corrosion protection methods, application of inhibitor is one of the most convenient methods for getting protection against corrosion of steel in acid media. The study of organic compounds as acid corrosion additives is a subject of continual interest due to several industrial applications such as acid pickling, descaling and oil well cleaning. Hence, several organic compounds containing nitrogen, oxygen and sulphur have been studied by several workers [1-8]. The efficiency of these inhibitors depends on chemical composition, structure of the inhibitor and nature as well as state of the metallic surface [9-11]. Most organic inhibitors are adsorbed on the metal surface by displacing water molecules and forming a compact barrier film [12]. The molecules that contain both nitrogen and sulfur in their structure are of particular importance, since these provide excellent inhibition when compared with the compounds that contain only S or N [13]. Most of the efficient inhibitors used in industries are organic compounds having multiple bonds in their molecules containing N and S atoms [14]. Dyes have been used as effective corrosion inhibitors in acid medium because they possess molecular structure recommended for investigation as possible corrosion inhibitor [15-20].

Synergistic corrosion inhibitor plays an important role both in theoretical and practical research [21]. Corrosion inhibition synergism takes place due to ion-pair interaction between organic cation and anion. Synergism between organic inhibitors and halide ions in metal corrosion in acid solution has been investigated by many researchers [22-24]. Synergistic inhibition effects of organic inhibitor/metallic ion mixture [25] and organic inhibitors/organic inhibitor mixture [26] on the corrosion of metals in acid media have also been reported.

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Azure A (AA) is a water soluble thiazin dye formed by the oxidation of methylene blue. It is strongly metachromatic (One dye exhibiting two different color reactions), and is used in making azure eosin stain for blood smear staining. In the present investigation, the inhibitive performance of AA on mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, at different temperatures has been studied by gravimetric, potentiodynamic polarization and electrochemical impedance techniques. The inhibition mechanism has been discussed on the basis of molecular properties such as dipole moment, energies of the highest occupied ( $E_{HOMO}$ ) and lowest unoccupied ( $E_{LUMO}$ ) molecular orbitals and Mulliken charges. The present work was also designed to understand the effect of synergistic inhibition between AA and  $\Gamma$  ions on the corrosion inhibition of mild steel in H<sub>2</sub>SO<sub>4</sub> medium.

#### MATERIALS AND METHODS

#### Materials and test solutions

Corrosion tests were performed on mild steel having the following composition (wt %) 0.016 P, 0.322 Si, 0.01 Al, 0.062 Cr, 0.05 Mn, 0.09 C, 0.05 S and the remainder iron (Fe). Azure A (AA), (3-amino-7-(dimethylamino) phenothiazin-5-ium chloride) was procured from Sigma Aldrich and used without further purification. The chemical structure of AA is shown in Fig. 1. A stock solution of AA (10 mM) was prepared by weighing an appropriate amount and dissolving in 0.5 M  $H_2SO_4$  and series of concentrations (0.5 mM - 5 mM) were prepared from this stock solution. The KI used was obtained from Merck, and a stock solution of 20 mM was prepared by weighing an appropriate amount of the salt and dissolving in 0.5 M  $H_2SO_4$ . All other chemicals used were of analytical grade purity.



Fig 1: Chemical structure of AA.

## Weight loss measurements

The test specimens were used in the form of coupons with a dimension of  $1 \text{ cm} \times 1 \text{ cm} \times 0.3 \text{ cm}$ . Before use, these coupons were polished with different emery paper up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol and acetone, and dried at room temperature. After weighing accurately, the specimens were immersed in 200 ml H<sub>2</sub>SO<sub>4</sub> with and without addition of different concentrations of AA. All the aggressive acid solutions were open to air. After 6 h of immersion the specimens were taken out, washed, dried and weighed accurately. Experiments were carried out in triplicate. The average weight loss of three parallel specimens was obtained. Relative weight losses of the coupons were used to calculate the percent inhibition efficiency IE (%). Then the tests were repeated with different concentrations of the inhibitor and at varying temperatures.

#### **Electrochemical studies**

Polarization and EIS experiments were carried out using a CHI660D electrochemical workstation. A three-electrode cell configuration consisting of rectangular mild steel specimen as working electrode (WE), a platinum electrode as counter (CE) and a saturated calomel electrode (SCE) as a reference was used. The specimen was pre-treated similarly as done in the gravimetric measurements. All experiments were carried out in 0.5 M  $H_2SO_4$  medium at 30 °C using a thermostatically controlled water bath (Weiber, India) under aerated condition and at different concentrations. Potentiodynamic polarization measurements were performed in the potential range from -900 to +500 mV with a scan rate of 0.4 mV s<sup>-1</sup>. The AC impedance measurements were performed in the frequency range of 10 to 0.05 kHz with signal amplitude of  $\pm$  10 mV. The equivalent circuit is shown in Fig. 2.



# Fig 2: Equivalent circuit diagram.

## Quantum chemical calculations

The molecular structure of AA was fully geometrically optimized by AM1 semi-empirical method (3-21G\*basis set) with Spartan' 08 V1.2.0. Four main related parameters, the energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), the energy of the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), energy gap ( $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$ ), and dipole moment ( $\mu$ ) were gained.



Fig 3: Variation of IE (%) as a function of temperature and concentration of AA.

#### **RESULTS AND DISCUSSION**

#### **Gravimetric measurements**

Table 1 shows the values of corrosion rate ( $C_R$ ), inhibition efficiency (IE%) and degree of surface coverage ( $\theta$ ) obtained from gravimetric measurements of mild steel in the absence and in the presence of various concentrations of AA at different temperatures in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution after 6 h of immersion. The values of  $C_R$  and IE (%) were calculated using the following equations:

$$C_{\rm R} = \frac{\Delta W}{St} \tag{1}$$

$$IE(\%) = \frac{(c_R)_{a} - (c_R)_{p}}{(c_R)_{a}} \times 100$$
<sup>(2)</sup>

where,  $\Delta W$  is the weight loss, S is the surface area of the specimen (cm<sup>2</sup>), t is immersion time (h), and  $C_{\rm R}$  is expressed in mg cm<sup>-2</sup> h<sup>-1</sup>.

				Temperature				
С,	30 °C		40 °C		50 °C		60 °C	
mM	$C_{\rm R}$ , mg cm <sup>-2</sup> h <sup>-1</sup>	IE (%)	$C_{\rm R}$ , mg cm <sup>-2</sup> h <sup>-1</sup>	IE (%)	$C_{\rm R}$ , mg cm <sup>-2</sup> h <sup>-1</sup>	IE (%)	$C_{\rm R}$ , mg cm <sup>-2</sup> h <sup>-1</sup>	IE (%)
0	1.991	-	4.518	-	7.713	-	15.403	-
0.5	0.698	64.94	1.657	63.32	2.597	66.33	5.426	64.77
1.0	0.624	68.66	1.380	69.46	2.196	71.53	4.561	70.39
1.5	0.553	72.23	1.234	72.69	2.015	73.88	4.209	72.67
2.0	0.463	76.75	1.119	75.23	1.827	76.31	3.699	75.98
2.5	0.390	80.41	0.950	78.97	1.491	80.67	2.995	80.55
3.0	0.299	84.98	0.704	84.42	1.097	85.78	2.429	84.23
4.0	0.177	91.13	0.402	91.10	0.621	91.95	1.475	90.42
5.0	0.155	92.21	0.383	91.52	0.601	92.20	1.289	91.63

Table 1: C<sub>R</sub> and IE (%) obtained from weight loss measurements of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing various concentrations of AA at different temperatures

The data in Table 1 reveals that the addition of AA decreases markedly the corrosion rate of mild steel. The IE (%) increases as the concentration of added AA is increased at all temperatures, and when the concentration reached to 5 mM, IE (%) of AA reached a high value of 92.21 at 30 °C, which represents excellent inhibitive ability (Fig. 3). This is due to the fact that, adsorption and the degree of surface coverage of inhibitor on the mild steel increases with the inhibitor concentration, thus the mild steel surface gets efficiently separated from the medium [27]. The protective property of this compound is probably due to the interaction between  $\pi$  electrons and hetero atoms with positively charged steel surface [28]. The results obtained from the weight loss measurements are in good agreement with those obtained from the electrochemical methods.

#### Potentiodynamic polarization

The anodic and cathodic polarization curves of mild steel electrode in 0.5 M  $H_2SO_4$  in the absence and presence of various concentrations of AA at 30 °C are shown in Fig. 4. The values of associated electrochemical parameters, such as corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves. The IE (%) was calculated using the following equation:

$$IE (\%) = \frac{(l_{corr})_{a} - (l_{corr})_{p}}{(l_{corr})_{a}} \times 100$$
(3)

where,  $(I_{corr})_a$  and  $(I_{corr})_p$  are the corrosion current density (mA cm<sup>-2</sup>) in the absence and presence of the inhibitor, respectively. It is clear from Fig. 4 that the presence of AA decreases both cathodic and anodic slopes with the increased inhibitor concentration. This could be attributed to the adsorption of inhibitor over the corroded metal surface [29]. Since both anodic dissolution of iron and hydrogen evolution were suppressed, the AA behaves like a mixed inhibitor [30].

 Table 2:  $E_{corr}$ ,  $R_{ct}$  and IE (%) obtained from polarization and impedance measurements for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing various concentrations of AA at 30 °C

C	E	IS	Polarization			
mM	$R_{\rm t},$ $\Omega {\rm cm}^2$	IE (%)	E <sub>corr</sub> , mV	$I_{\rm corr},$ mA cm <sup>-2</sup>	IE (%)	
0	34.3	-	-538	3.954	-	
0.5	105.0	67.32	-472	1.352	65.81	
1.0	111.3	69.17	-475	1.241	68.61	
1.5	129.0	73.40	-472	1.058	73.24	
2.0	160.2	78.58	-469	0.888	77.54	
2.5	190.1	81.95	-466	0.733	81.46	
3.0	255.3	86.56	-464	0.493	87.53	
4.0	321.8	89.34	-472	0.448	88.66	
5.0	381.0	90.99	-459	0.402	89.83	



Fig 4: Polarization curves for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at various concentrations of AA at 30 °C, and at a scan rate of 0.42 mV s<sup>-1</sup>.

The results of polarization measurements are summarized in Table 2. It is evident that  $I_{corr}$  decreases significantly with increasing concentration of AA, and the maximum IE (%) of 89.83 was reached at 5 mM of AA. This is because of increase in the blocked fraction of the metal surface by adsorption. Further, the concentration of AA has less effect on the  $E_{corr}$  which indicates that AA acts as a mixed type of inhibitor and the inhibition of AA on mild steel is caused by geometric blocking effect [31]. Ferreira and others [32-33] reported that, if the deviation in the  $E_{corr}$  is greater than 85 mV in inhibited system with respect to uninhibited, the inhibitor could be recognized as cathodic or anodic type where as if the deviation in  $E_{corr}$  is less than 85 mV, then it could be recognized as mixed type of inhibitor. In the present investigation, maximum deviation range was less than 85 mV, which implies that AA acts as a mixed type inhibitor.

#### **Electrochemical impedance spectroscopy**

The results of the potentiodynamic polarization experiments were further confirmed by impedance measurements, since EIS is a powerful tool in studying corrosion mechanism and adsorption isotherm. Generally, the Nyquist plots are analyzed in terms of equivalent circuit comprising of parallel capacitor and resistor, which include the solution resistance ( $R_s$ ) and double layer capacitance ( $C_{dl}$ ). The corrosion behavior of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of AA was investigated by impedance technique at 30 °C and results are represented by Nyquist plots as shown in Fig. 5.

The IE (%) was calculated using the charge transfer resistance as follows:

$$IE(\%) = \frac{\frac{1}{(R_{ct})_{a}} - \frac{1}{(R_{ct})_{p}}}{\frac{1}{(R_{ct})_{a}}} \times 100$$
(4)

where,  $(R_{ct})_a$  and  $(R_{ct})_p$  are charge transfer resistances in the absence and presence of inhibitor, respectively.

It is evident from the results that AA inhibited the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at all the concentrations used, and the IE (%) increased continuously with increasing concentration at 30 °C, and the maximum IE (%) of 90.99 was reached at 5 mM of AA and further increase in concentration did not cause any noticeable change in IE (%). The results in Table 2 indicate that the  $R_{ct}$  significantly increases and  $C_{dl}$  tends to decrease. This decrease in  $C_{dl}$  may probably due to decrease in local dielectric constant and/or an increase in the thickness of a protective layer at electrode surface which enhances the corrosion resistance of the mild steel [34]. The increase in  $R_{ct}$  values is attributed to the formation of protective film on the metal-solution interface [35-36]. These observations suggest that AA molecules function by adsorption at the metal surface thereby causing decrease in  $C_{dl}$  values and increase in  $R_{ct}$  values. The decrease in  $C_{dl}$  can also be explained on the basis that the double layer

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between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of the inhibitor on the electrode surface reduces its electrical capacity because of the displacement of the water molecules and consequently decreases in the number of active sites necessary for the corrosion reaction [37]. The decrease in this electrical capacity with increase in inhibitor concentration can be attributed to the formation of a protective layer on the electrode surface. The thickness of this protective layer increases with increase in inhibitor concentration, because more inhibitor molecules get adsorbed on the electrode surface resulting in a noticeable decrease in  $C_{\rm dl}$ . This trend is in accordance with Helmholtz model as given in Eq. (5) [38]:

$$C_{\rm dl} = (\varepsilon \varepsilon_0 A)/d$$

(5)

where, d is the thickness of the protective layer,  $\varepsilon$  the dielectric constant of the medium,  $\varepsilon_0$  the vacuum permittivity and A is the effective surface area of the electrode.



Fig 5: Nyquist plots of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of various concentration of AA at 30 °C.

#### **Effect of temperature**

In order to investigate the effect of temperature on the anticorrosion property of inhibitor in 0.5 M H<sub>2</sub>SO<sub>4</sub>, weightloss measurements were studied in the temperature range of 30 - 60 °C in the absence and presence of different concentrations of inhibitor during 6 h of immersion. The  $C_R$  gets increased with the rise in temperature in the uninhibited solution but in the presence of inhibitor,  $C_R$  gets highly reduced. Hence, inhibition efficiency decreases with the rise in temperature. It may be due to the fact that higher temperature accelerates hot-movement of the organic molecules and weakens the adsorption capacity of inhibitor on the metal surface [39]. Thermodynamic parameters such as the activation energy  $E_a^*$ , the entropy of activation  $\Delta S^*$  and the enthalpy of activation  $\Delta H^*$  for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of different concentrations AA were calculated using the following Arrhenius-type equation:

$$C_{\rm R} = A \, \exp\left(-\frac{E_{\rm a}^*}{RT}\right) \tag{6}$$

An alternative formulation of the Arrhenius equation is,

$$C_{\rm R} = \frac{RT}{Nh} \exp \frac{\Delta S^*}{R} \exp \left(-\frac{\Delta H^*}{RT}\right) \tag{7}$$

where, A is Arrhenius pre-exponential factor, h is Planck's constant, N is Avogadro's number, T is the absolute temperature and R is the universal gas constant. Using Eq. (6), and from a plot of the logarithm of  $C_{\rm R}$  versus 1/T (Fig. 6), the values of  $E_{\rm a}^*$  and k at various concentrations of AA were computed from slopes and intercepts, respectively. Further, using Eq. (7), plots of log  $(C_{\rm R}/T)$  versus 1/T gave straight lines (Fig. 7) with a slope of  $(-\Delta H^*/2.303R)$  and an intercept of  $[\log (R/Nh) + \Delta S^*/2.303R]$  from which the values of  $\Delta H^*$  and  $\Delta S^*$  were calculated and are listed in Table 3.

С,	$E_{\mathrm{a}}^{*}$ ,	I.	$\Delta H^*$ ,	$\Delta H^* = E_a^* - RT$	$\Delta S^*$ ,
mM	kJ mol <sup>-1</sup>	κ	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
0	56.01	9269543774	53.37	53.49	-62.94
0.5	55.41	2603181011	52.78	52.89	-73.50
1.0	53.96	1279838839	51.31	51.44	-79.40
1.5	55.20	1852866989	52.55	52.68	-76.32
2.0	56.47	2655768756	53.83	53.95	-73.41
2.5	55.16	1332070053	52.51	52.64	-79.07
3.0	56.44	1659861497	53.80	53.92	-77.32
4.5	57.01	1193313824	54.37	54.49	-80.98
5.0	57.13	1146523320	54.49	54.61	-80.31

Table 3: Activation parameters for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of AA

The lower or unchanged values of  $E_a^*$  in the inhibited systems compared to the blank suggests chemisorptions mechanism [35], whereas higher values of  $E_a^*$  indicates a physical adsorption mechanism [40]. In the present study the values of  $E_a^*$  in inhibited solution are almost same when compared to uninhibited acid solution (Table 3). This supports chemisorption of AA on mild steel surface. The positive sign of activation enthalpy ( $\Delta H^*$ ) reflects the endothermic nature of the steel dissolution process and that the dissolution of steel is difficult [41]. Large and negative values of ( $\Delta S^*$ ) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [42, 43].



Fig 6: Arrhenius plots of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of AA.

#### Adsorption isotherm

The degree of surface coverage ( $\theta$ ) as a function of the concentration of the inhibitor (*C*) was tested graphically by fitting it to various isotherms to find the best fit which describes this study. Langmuir adsorption isotherm was found to give the best description for AA on mild steel. According to this isotherm,  $\theta$  is related to the *C* and adsorption equilibrium constant  $K_{ads}$  as,

$$\frac{c}{\theta} = \frac{1}{K_{\rm ads}} + c \tag{8}$$

The plot of  $C/\theta$  versus C gave a straight line (Fig. 8) with a slope of around unity thereby confirming that the adsorption of AA on mild steel surface in H<sub>2</sub>SO<sub>4</sub> obeys the Langmuir adsorption isotherm.  $K_{ads}$  is related to the standard Gibb's free energy of adsorption  $\Delta G_{ads}$  as per the following equation:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \tag{9}$$

where, *R* is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution (mol  $L^{-1}$ ). This isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species.



1/T (K-1)

Fig 7: Alternative Arrhenius plots of mild steel dissolution in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of AA.



Fig 8: Langmuir adsorption isotherm of AA on mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different temperatures.

The negative values of  $\Delta G_{ads}$  suggest that the adsorption of inhibitor molecules onto steel surface is a spontaneous phenomenon. More negative values of  $\Delta G_{ads}$  suggest the strong interaction of the inhibitor molecules with the metal surface [44]. Generally, values of  $\Delta G_{ads}$  up to -20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption) while those negative values higher than -40 kJ/mol involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [45]. The value of  $\Delta G_{ads}$  is about -35 kJ mol<sup>-1</sup>, which probably means that both physisorption and chemisorption are taking place [46]. The positive value of  $\Delta S_{ads}$  (Table 4 and Fig. 9) obtained is attributed to increase in solvent entropy [47, 48]. The value of  $\Delta H_{ads}$  provides further information about the mechanism of corrosion inhibition. The endothermic adsorption process is ascribed unambiguously to chemisorption, an exothermic adsorption process may involve either physisorption or chemisorption or a combination of both the

processes [49]. In the present study, the negative values of  $\Delta H_{ads}$  obtained indicate a combination of both chemisorption and physisorption processes.

 Table 4: Thermodynamic parameters for adsorption of AA on mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different temperatures from Langmuir adsorption isotherm

Temperature, K	$\mathbb{R}^2$	$K_{\rm ads},$ L mol <sup>-1</sup>	$\Delta G_{ m ads},$ kJ mol <sup>-1</sup>	$\Delta H_{\rm ads},$ kJ mol <sup>-1</sup>	$\Delta S_{ads}$ , J mol <sup>-1</sup> K <sup>-1</sup>
303	0.993	2016.13	-29.26		
313	0.992	2036.66	-30.25	-14.62	64.66
323	0.993	2257.34	-31.49		
333	0.994	2304.15	-32.53		



Fig 9: Plot of  $\Delta G_{ads}$  versus absolute temperature.

#### Synergism considerations

The inhibition performance of AA on mild steel in 0.5 M  $H_2SO_4$  in the absence and presence of AA and also the combination of AA with KI was studied by gravimetric and electrochemical techniques at 30 °C. Inspection of Figs. 10 and 11 shows that  $C_R$  decreases in the presence of 0.5 mM AA as compared to the blank. The figures also showed that a further reduction in  $C_R$  was obtained on the addition of different concentrations of KI to AA.

The adsorption ability of halide ions on the metal surface is in the order  $\Gamma > Br^- > Cl^-[50]$ . The ease of adsorption shown by iodide ions may be due to less degree of hydration. Table 5 shows that the inhibition efficiency of AA synergistically increases on addition of different concentrations of KI. The improved inhibition efficiency of AA in the presence of halide ions is due to strong chemisorption of iodide ions on the metal surface [51, 52]. The cation is then adsorbed by coulombic attraction on the metal surface where iodide ions already get adsorbed by chemisorption. Stabilization of adsorbed iodide ions with cations leads to more surface coverage and thereby greater inhibition. Similar observation was reported by Larabi and Harek [53]

Table 5: IE (%) obtained from weight loss, polarization and impedance measurements of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing various concentrations of KI at 0.5 mM AA

С,	IE (%)					
mM	Weight loss	Polarization	EIS			
0.5 AA	64.94	65.81	67.32			
0.5 AA + 2.5 KI	76.24	78.51	79.85			
0.5 AA + 5.0 KI	83.87	86.89	86.00			
0.5 AA + 7.5 KI	86.40	89.58	90.25			
0.5 AA + 10.0 KI	88.12	92.77	93.76			



Fig 10: Polarization curves for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> with different concentrations KI.



Fig 11: Nyquist plots for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> with different concentrations KI.

#### Quantum chemical calculations

The selection of effective and appropriate inhibitors for the corrosion of metals has been widely carried out based on empirical approach [52-53]. In order to investigate the charge distribution of AA molecule, quantum chemical calculations were performed using the Spartan 08 V1.2.0 semi-empirical program.

Frontier orbital theory is useful in predicting the adsorption centers of the inhibitor responsible for the interaction with metal surface [54]. The optimized structure of AA is shown in Fig. 12a. A strong interaction between AA and metal surface is due to its planar structure, some key quantum chemical parameters were computed using the AM1 semi empirical method and these are listed in Table 6. These are mainly the energies of the highest occupied

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 $(E_{\text{HOMO}})$  and lowest unoccupied  $(E_{\text{LUMO}})$  molecular orbitals, dipole moment  $(\mu)$  and total energy  $(E_{\text{tot}})$ . These quantum chemical parameters were obtained after geometric optimization with respect to all nuclear coordinates.  $E_{\text{HOMO}}$  is associated with the electron donating ability of the molecule and high  $E_{\text{HOMO}}$  values indicate that the molecule has a tendency to donate orbital electrons to an appropriate acceptor with empty molecular orbital. Good corrosion inhibitors are usually those organic compounds which not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [55]. Similarly, low values of the energy gap ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) yields good inhibition efficiencies, because the energy required to remove an electron from the last occupied orbital will be low [56]. Low value of the dipole moment ( $\mu$ ) favors the accumulation of inhibitor molecules on the metallic surface [57]. The plots of HOMO and LUMO population are shown in Figs. 12b and 12c, respectively.



Fig 12: (a) Optimized structure, (b) HOMO and (c) LUMO of AA.



Fig 13: The Mulliken charge density of the AA molecule.

It could be seen that the frontier orbital HOMO are distributed around the thiazin and benzene rings with dimethyl groups while the LUMO are mainly on the benzene ring, which is attached to the methylamine group and carbon atoms which are adjacent to the nitrogen and sulphur atom of the thiazin ring. The use of Mulliken population analysis to find out the adsorption centers of inhibitors has been reported [57]. The Mulliken charge distribution of AA is presented in Fig. 13. It could be observed that nitrogen atoms and the benzene ring have higher charge densities and might form the adsorption centers. AA can interact with mild steel to form a good protective layer on the steel surface, thus slow down the corrosion of the metal in  $H_2SO_4$  solution.

Table 6:	Quantum	chemical	parameters for AA	
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Calculated parameters	μ(D)	$E_{\rm HOMO} ({\rm eV})$	$E_{\rm LUMO}~({\rm eV})$	E <sub>LUMO -HOMO</sub> (eV)	Etot (kJ/mol)
Values	7.18	- 8.01	-1.36	6.65	371.45

## CONCLUSION

- AA is an efficient corrosion inhibitor for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium.
- Adsorption of AA obeys the Langmuir adsorption isotherm.
- AA behaves as mixed type inhibitor.

• EIS results show that, as the inhibitor concentration increases the charge transfer resistance also increases and the double layer capacity decreases.

• The inhibition efficiency of AA is significantly enhanced in the presence of KI.

• Quantum chemical parameters also proved that AA acts as an efficient inhibitor for the corrosion of mild steel in 0.5 M  $\rm H_2SO_4$ .

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# REFERENCES

[1] M.A. Quraishi, D. Jamal, J. Appl. Electrochem., 2002, 32, 425.

[2] S. Vishwanatham, Anil Kumar, Corros. Rev., 2005, 23, 181.

[3] A. Popova, M. Christov, S. Raicheva, E. Sokolova, Corros. Sci., 2004, 46, 1333.

[4] A. J. Adbul Nassera, V. Rethina Girib, S. Karthikeyanc, K. N. Srinivasand and R. Karthikeyana *Der. Chemica. Sinica.*, **2012**, 3, 402.

- [5] N.O. Shaker, E.E.Badr and E.M. Kandee, Der. Chemica. Sinica., 2011, 2, 26.
- [6] K. Hart, N.C Oforka and A.O James, Advances in Applied Science Research, 2011, 2, 14.
- [7] K.N. Mohana, S.S. Shivakumar, A.M. Badiea, J. Korean. Chem. Soc., 2011, 55, 364.
- [8] S.S. Shivakumar, K.N. Mohana, Int. J. Electrochem. Sci., 2012, 7, 1620.
- [9] V.S. Sastry, Corrosion Inhibitors. Principles and Applications, John Wiley & Sons, New York, 1998.
- [10] F. Bentiss, M. Lagrence, M. Traisnel, Corrosion., 2000, 56, 733.
- [11] F. Bentiss, M. Traisnel, M. Lagrence, J. Appl. Electrochem., 2001, 31, 41.
- [12] S.S. Abd El Rehim, M.A.M. Ibrahim, K.F. Khaled, J. Appl. Electrochem., 1999, 29, 593.
- [13] N.A. Negm, Y.M. Elkholy, M.K. Zahran, S.M. Tawfik, Corros. Sci., 2010, 52, 3523.
- [14] J. De Damborenea, J.M. Bastidas, A.J. Vazquez, Electrochim. Acta., 1997, 42, 455.
- [15] H. Ashassi Sorkhabi, B. Masoumi, P. Ejbari, E. Asghari, J. Appl. Electrochem., 2009, 39, 1497.
- [16] R.A. Prabhua, T.V. Venkatesha, A.V. Shanbhag, J. Iran. Chem. Soc., 2009, 6, 353.
- [17] S.S. Al Juaid, Port. Electrochim. Acta., 2007, 25, 363.
- [18] M. Abdeli, N.P. Ahmadi, R.A. Khosroshahi, J. Solid. State. Electrochem., 2010, 14, 1317.
- [19] A.I. Onen, O.N. Maitera, J. Joseph, E.E. Ebenso, Int. J. Electrochem. Sci., 2011, 6, 2884.
- [20] E.E. Ebenso, H. Alemu, S.A. Umoren, I.B. Obot, J. Electrochem. Sci., 2008, 3, 1325.
- [21] G.N. Mu, X.M. Li, F. Li, Mater. Chem. Phys., 2004, 86, 59.
- [22] F. Bentiss, M. Bouanis, B. Mernari, M. Traisnel, M. Lagrenee, J. Appl. Electrochem., 2002, 32, 671.
- [23] E.E. Ebenso, Mater. Chem. Phys., 2003, 79, 58.
- [24] D.D.N. Singh, T.B. Singh, B. Gaur, Corros. Sci., 1995, 37, 1005.
- [25] M. Hosseini, S.F.L. Mertens, M.R. Arshadi, Corros. Sci., 2003, 45, 1473.
- [26] T.P. Zhao, G.N. Mu, Corros. Sci., 1999, 41, 1937.
- [27] A. Chetouani, B. Hammouti, A. Aouniti, N. Benchat, T. Benhadda, Prog. Org. Coat., 2002, 45, 373.
- [28] G.N. Mu, X.H. Li, Q. Qu, J. Zhou, Corros. Sci., 2006, 48, 445.
- [29] M.G. Hosseini, M. Ehteshamazadeh, T. Shahrabi, Electrochim. Acta., 2007, 495, 3680.
- [30] C. Cao, Corros. Sci., 1996, 38, 2073.
- [31] E.S. Ferreira, C. Giancomelli, F.C. Giacomelli, A. Spinelli, Mater. Chem. Phys., 2004, 83, 448.
- [32] W.H. Li, Q. He, C.L. Pei, B.R. Hou, J. Appl. Electrochim., 2008, 38, 289.
- [33] M. Lebrini, M. Traisnel, M. Lagrenee, B. Mernari, F. Bentiss, Corros. Sci., 2008, 50, 473.
- [34] E. McCafferty, N. Hackerman, S. Tsai, Corrosion., 1982, 38, 57.
- [35] F. Bentiss, M. Traisnel, M. Lagrenee, Corros. Sci., 2000, 42, 127.
- [36] F.B. Growcock, R.J. Jasinski, J. Electrochem. Soc., 1989, 136, 2310.
- [37] C. Bataillon, S. Brunet, Electrochim. Acta., 1994, 39, 455.
- [38] W. Li, X. Zhao, F. Liu, B. Hou, Corros. Sci., 2008, 50, 3261.
- [39] I. Dehri, M. Özcan, Mater. Chem. Phys., 2006, 98, 316.
- [40] A. Popova, Corros. Sci., 2007, 49, 2144.
- [41] N.M. Guan, L. Xueming, L. Fei, Mater. Chem. Phys., 2004, 86, 59.
- [42] N. Soltani, M. Behpour, S.M. Ghoreishi, H. Naeimi, Corros. Sci., 2010, 52, 1351.
- [43] M.K. Gomma, M.H. Wahden, Mater. Chem. Phys., 1995, 39, 209.
- [44] L. Tang, X. Li, L. Li, Q. Qu, G. Mu, G. Liu, Mater. Chem. Phys., 2005, 94, 353.
- [45] E. Bensajjay, S. Alehyen, M. El Achouri, S. Kertit, Anti-Corros. Meth. Mater., 2003, 50, 402.
- [46] P.M. Niamien, F.K. Essy, A. Trokourey, D. Sissouma, D. Diabate, Afr. J. Environ. Sci. Technol., 2011, 5, 641.
- [47] Emranuzzaman, T. Kumar, S. Vishwanatham, G. Udayabhanu, Corros. Eng. Sci. Technol., 2004, 39 327.
- [48] B. Ateya, B. El-Anadauli, F. El Nizamy, Corros., Sci., 1984, 24, 509.
- [49] S.A. Ali, A.M. El Shareef, R.F. Al Ghamdi, M.T. Saeed, Corros. Sci., 2005, 47, 2659.
- [50] G.K. Gomma, Mater. Chem. Phys., 1998, 55, 241.
- [51] Z.S. Syed, S. Muralidharan, S. Venkatakrishna Iyer, B. Muralidharan, T. Vasudevan, *Brit. Corros. J.*, **1998**, 297.
- [52] S.H. Sanad, A.A. Ismail, N.A. Mahmoud, J. Mater. Sci., 1992, 27, 5706.
- [53] L. Larabi, Y. Harek, M. Traisnel, A. Mansri, J. Appl. Electrochem., 2004, 34, 833.
- [54] L. Lukovits, E. Kalman, F. Zucchi, Corrosion., 2001, 57, 3.
- [55] A. Martnez Villafane, L. Martinez, D. Glossman Mitnik. Corros. Sci., 2006, 48, 4053.
- [56] D.Q. Zhang, Z.X An, Q.Y. Pan, L.X. Gao, G.D. Zhou, Corros. Sci., 2006, 48, 1437.
- [57] J. Fang, J. Li, J. Mol. Struct. (Theochem)., 2002, 593, 179.