Paper No. SS23



# Amino Acid based Imidazolium Zwitterions as novel and green corrosion inhibitors for mild steel: Experimental and DFT studies

**Jiyaul Haque** 

Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi -221005, India. Jiyaul 5555 5@gm ail.com

# M.A. Quraishi

Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi -221005, India.

# ABSTRACT

Three novel amino acids based corrosion inhibitors namely 2-(3-(carboxymethyl)-1H-imidazol-3ium-1-yl)acetate (AlZ-1),2-(3-(1-carboxyethyl)-1H-imidazol-3-ium-1-yl)propanoate (AlZ-2) and 2-(3-(1-carboxy-2-phenylethyl)-1H-imidazol-3-ium-1-yl)-3-phenylpropanoate (AlZ-3) were synthesized by condensing glyoxal, formaldehyde and amino acids, and characterized. The corrosion inhibition performance of synthesized inhibitors was studied by electrochemical impedance (EIS) methods. Among the studied inhibitors, AlZ-3 showed the maximum IE of 94.76% at a concentration as low as 0.55 mM (200 ppm). The results of potentiodynamic study reveal that AlZ-1 acts as cathodic inhibitor while AlZ-2 and AlZ-3 act as mixed type inhibitors. The results of EIS studies showed that in the presence of inhibitors, polarization resistance increased and C<sub>dl</sub> decreased due adsorption of inhibitors at the metal surface. The result of scanning electron microscope (SEM) supported the formation of inhibitors film on the metal surface. The quantum chemical parameters were used to study the reactivity and adsorption behavior of zwitterions.

Keywords: Mild Steel, Corrosion inhibition, Quantum chemical calculation, imidazolium zwitterions.

#### INTRODUCTION

Each country loses 3-5% of its GDP on account of corrosion. The global economic loss due to corrosion is approximately \$2.5 trillion estimated by National association of corrosion engineers (NACE) in 2016 [1]. Mild steel finds wide applications in various industries, because of its low cost and excellent mechanical strength. However, it undergoes severe corrosion when it is exposed to the acid solution during pickling and acid cleaning, descaling and oil-well acidification [2, 3]. Inhibitors are added to acid solutions to prevent metal dissolution. The use of inhibitors is one of the most practical

NIGIS \* CORCON 2017 \* 17 – 20 September 2017 \* Mumbai,India Copyright 2017 by NIGIS. The material presented and the views expressed in this paper are solely those of the author(s) and do not necessarily by NIGIS. methods to protect metals from corrosion. Most of the synthetic inhibitors are toxic and cause health hazards [4]. Therefore, their replacement by the environmentally benign inhibitors is desirable. Amino acids have been reported as effective corrosion inhibitors [5-8]. In view of the high performance of the condensation product histidine and cysteine, we have synthesized three condensation products namely AIZ-1, AIZ-2 and AIZ-3 and evaluated them as corrosion inhibitors for mild steel in 1 M HCI. The corrosion inhibition effect of these compounds (AIZs) has been studied by electrochemical impedance spectroscopy (EIS) methods.

#### **EXPERIMENTAL PROCEDURE**

The mild steel specimens having chemical composition (wt %) C 0.076%, Si 0.026%, Mn 0.192, P 0.012%, Cr 0.050%, Ni 0.050%, Al 0.023% and Cu 0.135% and Fe 99.30% were used for gravimetric and electrochemical experiments. The mild steel specimens were abraded by SiC abrasive papers (from grade 600 to 1200), rinsed with distilled water, degreased in acetone and dried in hot air and stored in moisture free desiccators before their use [9]. The test solution of 1M HCl was prepared by the dilution of analytical grade hydrochloric acid (HCl, 37 %, Fisher Scientific) with double distilled water. The investigated inhibitor has been synthesized in the lab by using the analytically pure chemical, shown in Figure. 1.



#### Figure 1: Synthetic scheme of studied AIZs.

# **Corrosion test**

#### **Electrochemical test**

The conventional three-electrode glass cell consisting of mild steel specimen with the  $1 \text{cm}^2$  (onesided) exposure area was used as working electrode (WE), platinum foil counter electrode (CE) and saturated calomel reference electrode (RE) were used for all the electrochemical experiments. All the electrochemical experiments performed by using the Gamry Potentiostat/Galvanostat (Model G-300) instrument and Gamry Chem Analyst 5.0 software was used for fitting and analyzing the electrochemical data. The EIS experiment was carried out in the frequency range 100 kHz to 0.01 Hz with sinusoidal amplitude of 10 mV Ac signal. Polarization resistance ( $R_p$ ), double layer capacitances ( $C_{dl}$ ) and other parameters were calculated by fitting Nyquist plot. The inhibition efficiency was calculated by applied the following equation:

$$IE(\%) \xrightarrow[p]{R_i R_0} 1$$
$$\frac{R_i}{\frac{R_i}{p}} 0$$

(1)

where  $R^{0_{p}}$  and  $R^{i_{p}}$  are the polarization resistances in the absence and presence of different concentrations of AIZ molecules, respectively.

#### Quantum chemical calculation

Quantum chemical calculations were performed by using Gaussian 09 suited program [10]. The complete geometry optimization was conducted by the DFT with Becke's three parameter

exchange functional with the Lee–Yang–Paar correlation functional (B3LYP) [11,12]. The calculation was carried out by using the basis set 6-311G(d,p) for protonated forms. The quantum chemical parameters such as the energy of highest occupied molecular orbital ( $E_{HOMO}$ ), and lowest unoccupied molecular orbital ( $E_{LUMO}$ ) have been calculated by optimized molecular structures of AIZs. Other Quantum parameters like Energy gap ( $E_{LUMO} = E_{HOMO}$ ), hardness ( $\eta$ ), softness ( $\sigma$ ),

electronegativity ( $\chi$ ) and fraction of electrons transfer ( $\Delta N$ ) were calculated by using the following equations:

$$\eta = \frac{1}{2} (E_{LUMO} - E_{HOMO})$$
(2)
$$1$$

$$2^{E} LUMO E HOMO}$$
N
$$F^{e} inh inh}$$
2
$$2($$
Fe inh Fe inh )

# (3)

(4)

In equation (4), the electronegativity of iron metal surface  $\chi$ Fe is replaced by the work function ( $\phi$ ), previously described [10, 13]. The  $\phi$  values obtained from DFT calculation are 3.91, 4.82 and 3.88 eV for the Fe (100), Fe (110) and Fe (111), respectively. Herein, we have chosen Fe (110) surface due to its high stabilization energy and packed structure.

NIGIS \* CORCON 2017 \* 17 – 20 September 2017 \* Mumbai, India Copyright 2017 by NIGIS. The material presented and the views expressed in this paper are solely those of the author(s) and do not necessarily by NIGIS.

# RESULTS

#### **Electrochemical study (EIS)**

Figure 2 show the Nyquist plots for mild steel with and without different concentrations of AlZs. Nyquist plots consist of a depressed capacitive loop along with the real axis and their size increases with increasing the concentration of inhibitor molecules (Figure 2), indicating that the corrosion of mild steel in 1M hydrochloric acid solution is controlled by polarization resistance ( $R_p$ ) [14]. The equivalent circuit model used to interpret the impedance results is given in Figure 3. It consists of solution resistance ( $R_p$ ), polarization resistance ( $R_p$ ) and constant phase element (CPE) [15]. CPE is used in place of capacitor in order to accurately fit the circuit. CPE can be represented by the following equation:



(5)where Y0 and n are the magnitude and exponent (phase shift) of the CPE, respectively,  $j^2 = -1$  is an imaginary number and  $\omega$  is the angular frequency. Properties of CPE depends on the value of n. From the Table 1, it can be seen that the values of n vary from 0.827 to 0.886, which suggest that the surface inhomogeneity decreases due to adsorption of AIZ molecules on the mild steel surface [16]. The values of EIS parameters such as R<sub>P</sub>, CPE, Y<sup>0</sup> and n obtained by fitting the EIS spectra are listed in Table 1. The values of C<sub>d</sub> can be calculated from the CPE parameters Y and n using the following equation:

C Y <sup>n 1</sup> <sup>dl</sup> sin( n( / 2))

As shown in Table 1, the value of  $R_p$  increases and  $C_d$  decreases with increasing the inhibitor concentration, which is attributed to increase in the thickness of the electric double layer on the metal/solution interface and/or decrease in the value of dielectric constant due to the displacement of pre-adsorbed water molecules by the inhibitors. From Table 1, the inhibition performance order of AIZ molecules is AIZ-3 > AIZ-2 > AIZ-1.

Table 1: EIS parameters obtained for mild steel in 1 M HCl in absence and presence of different concentration of AIZs

Inhibitors	Conc	Rs	Rp	n	Cdl	IE (%)
	(mM)	$(\Omega \text{ cm}^2)$	(Ω cm <sup>2</sup> )		(µF cm <sup>-2</sup> )	
Blank		1.12	10.7	0.83	106.21	
AIZ-1	0.14	1.01	49.0	0.83	102.66	78.16
	0.27	0.67	82.9	0.76	100.64	87.09
	0.41	0.66	105.7	0.74	96.63	89.88
	0.55	0.64	144.4	0.71	76.20	92.59
AIZ-2	0.14	0.51	69.9	0.86	64.56	84.69
	0.27	0.62	114.2	0.86	34.99	90.63
	0.41	0.45	155.6	0.87	32.15	93.12
	0.55	0.77	171.9	0.88	29.52	93.77
AIZ-3	0.14	0.78	84.7	0.86	105.12	87.36
	0.27	0.85	126.0	0.87	63.83	91.50
	0.41	1.02	149.2	0.88	54.92	92.82
	0.55	0.80	204.4	0.89	98.21	94.76



Fig. 2: Nyquist plot for mild steel in 1 M HCl without and with different concentrations of AIZs 1M hydrochloric acid solution at 308K.



Fig. 3: Equivalent circuit model used for fit and analyzed electrochemical data

# Surface Study (SEM analysis)

Scanning electron microscope (SEM-EDX), Ziess Evo 50 XVP was used to study the changes occurring on metal surface along with the elemental composition. The SEM images were taken at 500x magnification. Scanning electron microscopic (SEM) images of uninhibited and inhibited mild steel surfaces in 1 M HCl solution are shown in Figure 4. Figure 4a represents the SEM image of the uninhibited metallic specimen which is drastically damaged and corroded due to free acid attack in the absence of inhibitors. However, in the presence of inhibitors at their optimum concentration, the surface morphologies of the metallic specimens (Figure 4b-d) were remarkably improved, due to the formation of the protective film by AIZ molecules on the metallic surface which separates the

metals from corrosive environments and protects from corrosion.



Figure. 4: SEM images of mild steel: (a) in absence of AIZs and in the presence of 0.55 mM of (b) AIZ-1, (c) AIZ-2, and (d) AIZ-3.

# Theoretical studies

#### Quantum chemical calculation

Quantum chemical study using DFT method is an important theoretical tool to study the reactivity of the inhibitor molecules [17]. AIZ molecules exist in cationic and anionic forms depending upon the pH of the medium [18, 19]. In highly acidic solution such as 1M HCI, these molecules exist predominantly in protonated forms. In view of this, DFT based quantum chemical calculations were carried out for protonated forms of AIZ molecules in aqueous phase. The geometrically optimized structures are depicted in Figure 5 and HOMOs, LUMOs of protonated form of AIZ molecules are shown in Figure 6. The quantum chemical parameters such as EHOMO, ELUMO,  $\Delta E$  = EHOMO-ELUMO hardness (n), softness ( $\sigma$ ), electronegativity ( $\chi$ ) and fraction of electrons transfer (N<sub>110</sub>) for protonated form of inhibitors are presented in Table 2. The inhibition effect of inhibitor molecule is usually attributed to the adsorption of AIZ molecules on the metal surface. The analysis of frontier molecular orbital (HOMO and LUMO) is useful to predict the adsorption center of AIZ molecules responsible for the interaction with metal surface [20]. HOMO and LUMO are associated with the electron donor and acceptor ability of AIZ molecules, respectively. Molecules with higher value of EHOMO (less negative) and lower value of ELUMO (more negative) show more donor and acceptor tendency of electrons with appropriate metal d-orbital, respectively [21]. From Figure 6, it can be observed that HOMO are distributed over the imidazole ring in all the AIZ molecules. Therefore, the

imidazole ring is responsible for donating the electron to the available vacant 3d orbital of Fe (110). LUMOs are mainly distributed over the carboxylic group of the inhibitor molecules.



Figure .5 The optimized structures of protonated AIZ inhibitors.