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## Highly functionalized epoxy macromolecule as a anti-corrosive material for carbon steel: Computational (DFT, MDS), surface (SEM-EDS) and electrochemical (OCP, PDP, EIS) studies

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#### Abstract

In present study, a tetra-functionalized aromatic epoxy pre-polymer namely, 4,4'oxybis(N,N-bis(oxiran-2-ylmethyl)aniline) (AA2) was synthesized and established as corrosion inhibitor for carbon steel corrosion in 1 M HCl medium. The prepolymer was characterized by proton nuclear magnetic resonance (<sup>1</sup>H NMR) and Fouriertransform infrared spectroscopy (FT-IR) spectral techniques and its inhibition property was demonstrated using electrochemical open circuit potential (OCP), potentiodynamic polarization(PDP) and electrochemical impedance spectroscopy (EIS), surface scanning electron microscopy (SEM) analysis coupled with energy dispersive spectroscopy (EDS) analysis and computational density functional theory

(DFT) and molecular dynamic (MD) simulations methods. Electrochemical studies demonstrate that AA2 acts as sensibly good inhibitor for carbon steel in 1 M HCl medium and showed highest efficiency of as high as 91.3% at 10<sup>-3</sup>M.The PDP results show that AA2 behaves as predominantly cathodic type of inhibitor.SEM analysis coupled with EDS showed that AA2 forms surface protective films and isolates the metal from aggressive solution. DFT studies suggest that both neutral as well as cationic forms of the AA2 strongly interact with metallic surface using two aromatic and four oxirane rings. Molecular dynamic simulations (MDS) study showed that AA2 adsorb strongly on metallic surface using their electron rich centers and acquires the parallel or flat orientation. Outcomes of the experimental (SEM-EDS, OCP, EIS and PDP) and computational (DFT and MDS) studies were in excellent concurrence.

*Keywords:* Epoxy prepolymer inhibitor, electrochemical, cathodic inhibitor, Langmuir adsorption isotherm and computational studies.

### **1. Introduction**

Steel alloys have constantly been the materials of enormous significance for an assortment of engineering applications for the reason that of their fashionable and outstanding mechanical properties[1,2]. However, they suffer severe attack in corrosive environments (acid solutions) especially HCl and H<sub>2</sub>SO<sub>4</sub> solutions which are repeatedly being utilized in acid pickling, acid descaling, acid cleaning, etc. processes [3,4]. Therefore, these engineering and industrial processes require the addition of corrosion inhibitors in aggressive solutions [5, 6]. Use of organic compounds as corrosion inhibitors is one of frequent methods against the corrosion because of their economic and inhibition effectiveness along with ease of synthesis and application. These compounds adsorb on metallic surface through their polar functional groups including amines, amides, diamines, polyols, diols, ketones, aromatic rings, etc. [7-9]. Here, we demonstrated the anti-corrosive property of an aromatic epoxy prepolymer namely, 4,4'-oxybis (N,N-bis(oxiran-2-ylmethyl)aniline) (AA2) on acidic dissolution of carbon steel using several experimental and computational techniques. The organic aromatic epoxy prepolymer contains several electron rich sites in the form of nitrogen (N), oxygen (O) and  $\pi$ -electrons through which AA2 can adsorbs effectually and slowdown or retards the corrosion attack thereafter. Owing to its high molecular size, AA2 covers larger surface area and behaves as good anti-corrosive compound. Four peripheral polar groups enhance the AA2 solubility in the electrolyte (1M HCl). Inhibition effect of the AA2 was investigated using computation and experimental techniques and the results were in good agreement.

#### 2. Experimental

### 2.1. Materials and methods

The materials used in this study such as 4,4'-oxydianiline (purity of 97%), epichlorohydrin (purity of 99%) and triethylamine (purity of  $\geq$ 99.5%) were purchased from Sigma-Aldrich. Carbon steel strips containing C 0.11 wt.%, Si 0.24 wt. %, Mn 0.47 wt.%, Cr 0.12 wt. %, Mo 0.02 wt.%, Ni 0.1 wt.%, Al 0.03 wt.%, Cu 0.14, Co <0.0012 wt. %, V <0.003 wt.%, W 0.06 wt. %[10].

The corrosive solution of 1 M HCl was prepared by diluting the appropriate amount of concentrated HCl (37%) with distilled water. The range of concentration for the tested inhibitor was from  $10^{-3}$  to  $10^{-6}$  mol L<sup>-1</sup>. This range of concentrations was determined after the study of the solubility of the tetra-functional epoxy macromolecule (AA2) in the corrosive medium.

### 2.2. Chemical synthesis of AA2

A mixture of organic compound (aromatic diamine)  $(2.0 \times 10^{-2} \text{ mol})$  and ethanol (20 mL) was put in a bicol equipped with a condenser and a dropping funnel. After dissolving the aromatic diamine, 4 mL of epichlorohydrin was poured with invariable magnetic thrilling. The resulting reaction mixture was heated at 70 °C for 4 h. Then, 5mL of triethylamine was added to the reaction mixture. Stirring was continued for a further 3 hours at 40 °C. Viscous resin was obtained by concentrating the resulting solution on a rotary evaporator. Scheme for AA2 synthesis is given Fig. <u>1</u>. TheAA2 synthesis was verified by <sup>1</sup>H NMR (using Bruker AVANCE 300 MHz)and FT-IR spectroscopic methods and corresponding spectra are given in Figs. SI <u>1</u> and SI2and Table SI <u>1</u>.

### **2.3. Electrochemical test**

Electrochemical study of carbon steel dissolution in 1M HCl in the absence and presence of AA2was performed using Potentiostat SP 200 device as described in our previous studies [11, 12]. The device is connected by means of a three-electrode arrangement consisting of pure Pt as the auxiliary or assisting electrode (CE), saturated calomel the same as the reference electrode (SCE) and carbon steel panels the same as the working electrode (WE). Prior to starting the electrochemical

experiments, the WE permitted to corrode liberally with and without AA2 for 1800 second in order to acquire the establishment of OCP (open circuit potential). The EIS measurements were performed over a frequency range of 100 kHz to 10 mHz, using 10 mV amplitude. The PDP curves were measured at a scan rate of 1 mV/s from -800 to 0 mV versus SCE.

### 2.4. SEM characterization

SEM-EDS study was carried out using model S3000H, Hitachi-Field Emission for carbon steel surfaces corrode for 12 h in 1M HCl solution.

### 2.5. Theoretical study

DFT calculations were accomplished with the Gaussian 09 program. Geometry optimization in the aqueous phase for the AA1 was completely optimized atB3LYP/6-31G (d, p) level of the theory[13].

The molecular dynamics (MD) simulation was performed using Forcite module of Materials Studio 8.0 program developed by BIOVIA Inc. It was carried out in a simulation box (2.48 nm  $\times$  2.48 nm  $\times$  4.71 nm) with periodic boundary conditions. The box consisted of a lower Fe slab and a upper solvent layer (containing 800 water molecules and one inhibitor molecule)[14].

#### 3. Result and discussion

### 3.1. Electrochemical Study

Open circuit potential (OCP) can be defined the same as "potential originated over the working electrode (carbon steel in this case) without applying any external current or potential". Fig. 2, represents the OCP versus time curves for WE corrosion of the bare carbon steel substrate and presence the different concentrations of AA2.For better interpretation and reliability of the OCP curves, the OCP studies for carbon steel dissolution in 1M HCl were carried out for 1800 s. Generally, straight OCP versus time curves suggest the dissolution of surface metal oxide layer(s) and adsorption of the corrosion inhibitor(s) that interface of metal and electrolyte [15]. From Figure 2, it can be clearly seen that OCP versus time curves are almost straight throughout the experiments for different concentrations AA2 in their absence. This observation suggests that shift in OCP versus time curves of inhibited specimens with respect to the uninhibited once gives information about the nature of corrosion inhibitor. Visualization show that OCP versus time curves for the metallic specimens inhibited by AA2 are shifted towards more negative (cathodic) direction which reveals that AA2 is mainly acts as cathodic type of corrosion inhibitors [16].

Tafel curves and respective polarization indices are shown in Fig. 3and Table 1, respectively. Using  $i_{corr}$ , efficiency of protection ( $\eta_{PDP}$  %) was determined by the following Eq. (1):

$$\eta_{PDP} (\%) = \left(1 - \frac{i_{corr}}{i_{corr}^0}\right) \times 100 \quad (1)$$

Whereas,  $i_{corr}^0$  are the current densities for steel corrosion in the absence and presence of AA2 in HCl solution, respectively.

Inspection showed that icorr value decreased from 916.6 to 81.66  $\mu$ .cm<sup>-2</sup>in the presence of 10<sup>-3</sup> M concentration of AA2.The decrease in *i*<sub>corr</sub> value in the presence of AA2 is attributed to the blocking of the surface active sites [13]. Presence of peripheral polar groups, nitrogen and oxygen atoms enhance the adsorption of AA2 on the metallic surface. More so, presence of these hydrophilic moieties enhances the solubility in the polar electrolytic solution of 1M HCl.

Nyquist plots for steel acidic dissolution in 1M HCl is shown in Fig. 4. Formation of single semicircle with and without AA2 suggests that dissolution of the working electrode is a charge transfer process [17]. Surface heterogeneity causes the imperfection in the semicircle. Increased diameter of semicircle also indicates that AA2 adsorbs at metal/ electrolyte interfaces and acts as interface type of inhibitor.

Equivalent circuit engaged intended for appropriately analyzing the EIS data is shown in Fig. 5. The CPE is defined as the below Eq.  $(\underline{2})$  [18]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^{\alpha}} (2)$$

Here, symbols have their typical meaning [19]. The capacitance values ( $C_{dl}$ ) is calculated using Eq. (3) [20]:

$$C_{dl} = Y_0(\omega_{max})^{n-1}(3)$$

The polarization resistance parameters were used to calculate the corrosion inhibition efficiency ( $\eta_{\text{EIS}}$ %) based on the following Eq (<u>4</u>):

$$\eta_{EIS} (\%) = \left(1 - \frac{R_P^0}{R_P}\right) \times 100 \quad (4)$$

Results showed that presence of AA2 enhances the polarization resistance value and corresponding increase in the inhibition efficiency [21]. AA2 showed highest value of 91.3 % at  $10^{-3}$ M concentration. Decrease in the values of  $C_{dl}$  in the presence of AA2

suggests that surface smoothness is increasing because of the AA2 adsorption at the interfaces[22]. This assumption was further supported by increased value of phase angle values in the Bode plots (Fig. 6) for steel acidic dissolution [22].

### 3.2. Morphological analysis

SEM-EDS images for the working electrode surfaces are presented in Fig. <u>7</u>. It can be seen that without AA2 surface was highly damaged and corroded with very high surface imperfection. However, in the presence of AA2 surface morphology is greatly improved due to AA2 adsorption over the metallic surface.

#### **3.3. Adsorption studies**

Nature of carbon steel and AA2 interaction can be demonstrated using adsorption isotherm and Langmuir adsorption isotherm is best model that can be presented as follows[23].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}(5)$$

All symbols have their typical meaning. Graphs between  $C_{inh}$  and  $C_{inh}/\theta$  is shown in Fig. SI<u>3</u>. The  $\Delta G_{ads}$  are calculated using Eq. (6) [24] :

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G_{ads}}{RT}\right) (6)$$

It is well known that value of  $\Delta G_{ads}$  the order of lower than -40 kJ/mol were reported as chemisorption owing to the formation of covalent bond between organic inhibitors and to the metallic surface [25]. If the  $\Delta G_{ads}$  value is around or higher than -20 kJ/mol indicates a physisorption [26]. Results revealed that AA2 adsorption mainly obeyed the chemisorption (Table SI<u>2</u>).

#### **3.4. Effect of temperature**

The PDP study was conducted at 298, 308, 318 and 328 K temperature and corresponding outcomes are given in Fig. <u>8</u> and Table <u>3</u>. Effect of temperature can be presented as follows Eqs (<u>7</u>) and (<u>8</u>)[27]:

$$i_{corr} = A. \exp\left(-\frac{E_a}{RT}\right)(7)$$

$$i_{corr} = \frac{RT}{hN} exp\left(\frac{\Delta S_a}{R}\right) exp\left(-\frac{\Delta H_a}{RT}\right) (8)$$

where A is the pre-exponential factor,  $\Delta H_a$  is the enthalpy,  $\Delta S_a$  is the entropy of activation, *T* is the absolute temperature in Kelvin, *h* is the Plank constant, N is the Avogadro number, and *R* the molar gas constant. Results are presented in Fig. SI <u>4</u> and Table SI <u>3</u>. Careful observation showed that value of  $E_a$  in the presence of the AA2 is higher than in their absence. The studied AA2 retard corrosion at room temperature, but inhibition is diminished at an elevated temperature. The decrease in the corrosion rate is mostly determined by the  $E_a$  [28].Moreover, the positive values of  $\Delta H_a$  showed that the corrosion process is endothermic. The higher value of  $\Delta S_a$  in the presence of AA2 is attributed to increase in solvent entropy, which drives the adsorption of inhibitors on the metal surface [29].

#### 4. Theoretical study

Recently, quantum chemical calculation facilitated the development of adequate corrosion inhibitors. DFT investigates globally and locally all the probable donation and accepting interaction of the inhibitor molecule as well as every atom in it. DFT extensively investigated evidence that for an inhibitor might be adsorbed to show corrosion inhibition characteristic. More specifically, the donation-accepting type interaction that is accountable for adsorption on the favored surface. So that, DFT provides the connection of molecular structure or characteristics with the ability of the inhibitor molecule to inhibit the surfaces from corrosion. Accordingly, for this study, the global and local quantum chemical calculations have been performed using DFT method at the B3LYP/6-31+G(d,p) level of theory in aqueous solution using PCM model.

### 4.1. Global and Local quantum descriptors of the neutral AA2

The optimized geometrical structure and the electrostatic potential map of the neutral species of the AA2 molecule are presented in Figure 9. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the AA2 molecule, as well as their energy values and the energy gap between them are shown in Figure 10. The calculated quantum chemical descriptors such as  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , energy gap  $(\Delta E)$ , dipole moment ( $\mu$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness(S), electrophilicity ( $\omega$ ), electron accepting power ( $\omega$ ), electron donating power ( $\omega$ ), netelectrophilicity ( $\Delta \omega^{\pm}$ ), Charge transfer model for donation and back-donation

of charges ( $\Delta E_{b-d}$ ), Number of transferred electrons ( $\Delta N_{110}$ ), number of electron transfer electron from metal to inhibitor( $\Delta N_{max}$ ), and the initial molecule-metal interaction energy( $\Delta \psi$ ) are collected in Table 4. The equations used to calculate the above mentioned parameters are given as a footnote under Table 4.

Figure 9 shows that the optimized structure of the inhibitor AA2 has a non-planar geometry in location, indicating that it is not adsorbed in horizontal location on the metal surface. Hence, the question to be addressed here is how improbable amount of inhibition efficiency may be expected by the inhibitor AA2. Figure 10affirmed that electron density of the HOMO is dispersed over the entire molecule, whereas considerable electron density is distributed in LUMO over the middle part of the molecule (the two aromatic rings). These observations are also confirmed when the ESP map is considered (Figure 9). Therefore, the middle part of the molecule shows a dual behavior; donor-acceptor property, which facilitates the adsorption of the inhibitor molecule over the metal surface and consequently increases the inhibition efficiency of the inhibitor molecule[9, 10, 11, 30-36]. More specifically, the energy of the  $E_{\text{HOMO}}$  is commonly correlated with the ability of the inhibitor molecule to donate its electrons to the vacant d orbital of the metal. Thus, the higher the  $E_{HOMO}$  and the lower the  $E_{\text{LUMO}}$  values, the better inhibition efficiency of the inhibitor [37-39]. It is clearly obvious from Table 4 that the inhibitor molecule has higher  $E_{HOMO}$  and lower  $E_{\rm LUMO}$  value compared with those reported for some previously published molecules [7,30,40]. In order to earn additional information, whether the investigated AA2 molecule adequate to donate the electron or not, the values of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  can be used to calculate the above mentioned global quantum descriptors [41]. One of the most important global descriptors is the energy gap, which can be used to elucidate the reactivity of the inhibitor molecule. It was reported that lower values of energy gap indicates a high chemical reactivity and inhibition efficiencies of the inhibitor molecules [37-39]. A careful inspection of Table 4 and Figure 10 shows that the value of energy gap if the titled inhibitor is small ( $\Delta E = 4.405 \text{ eV}$ ), which displays that the AA2easily polarized and get adsorbed.

Lower values of electronegativity and hardness also indicate that the inhibitor under probe is highly reactive molecule and can transfer as well as accept electrons during metal-inhibitor interactions. According to our results (Table 5), the inhibitor under

probe has a negative  $\Delta E_{\text{back-donation}}$ , which demonstrates a highly efficient inhibition. It is also shown the rest of the quantum global parameters reflect a good inhibition efficiency of the investigated inhibitor, which is a good agreement with experimental results. Furthermore, fraction of electron transferred ( $\Delta N_{110}$ ) between the metal surface and the inhibitor molecule AA2 is calculated using Eq. (9).

$$\Delta N_{110} = \frac{(\varphi_{Fe} - \chi_{Fe})}{2(\eta_{Fe} + \eta_{inh})} (9)$$

where,  $\phi$ ,  $\chi_{inh}$  correspond to work function of iron and electronegativity of the inhibitor, while  $\eta_{\text{Fe}}$  and  $\eta_{\text{inh}}$  corresponds to hardness of Fe and inhibitor molecule, respectively. It was reported that the obtained DFT derived  $\varphi$  values for Fe(100), Fe(110) and Fe(111) planes are 3.91, 4.82 and 3.88 eV, respectively[42]. For this study, the Fe(110) plane is treated due to its packed surface and higher stabilization energy. The results obtained are also listed in Table 4. It is well known that electrons transfer takes place from AA2 molecule Fe(110) surface when  $\Delta N_{100} > 0$  and vice versa[42-44]. Additionally, it was proposed that the ability of the inhibitor to give electrons increases when the  $\Delta N_{100} < 3.6$  [45].Careful inspection of Table 4 affirms that the calculated  $\Delta N_{100}$  value is positive (0.4177) and less than 3.6. Therefore, the AA2 inhibitor may transfer its electron to the metallic surface, which in turn facilitates the adsorption of the AA2 on the Fe(110) surface. Moreover, higher softness (S) value demonstrates the high inhibition efficiency of the AA2 molecule. The calculated softness value of the AA2 inhibitor (S =  $0.454 \text{ eV}^{-1}$ ) is quite good enough compared with those reported for a previously published inhibitors [7,9,10,30,40,46].

Finally, it was also reported that higher value of dipole moment enhances the dipoledipole interactions between the metallic surface and the adsorbed inhibitor, resulting in better adsorption and, in turn, higher inhibition effect [47].Our results (Table 4) demonstrate that the dipole moment value of the investigated inhibitor molecule is 0.803 Debye, which is smaller than that of water (1.8546 Debye).These results reveal that the dipole-dipole interactions between the neutral AA2 and the Fe(110) surface is week.

### 4.2. Fukui indices study

As known, the responsible interactions in the inhibition operation are the donoracceptor processes. In these interactions, the inhibitor molecules are adsorbed on the surface of the metal. Hence, it is very valuable to examine the atoms in the molecule that participate in this type of interaction. For this purposes, the condensed Fukui functions in a molecule with N electron were proposed by Yang and Mortier [48]. In the current study, the Fukui Functions (FFs) was used to analyze the reactive sites of the investigated inhibitor molecule. The Natural Population Analysis (NPA) as implemented in G09 [49] was adopted to calculate the FFs. All NBO single point calculations for neutral, cationic and anionic species were performed using geometrical structures of the studied inhibitors at the same level of theory. The sites for nucleophilic  $(f_k^+)$  and electrophilic  $(f_k^-)$  can be evaluated in terms of the electronic populations as Eqs. (10) and (11):

$$f_k^+(k) = q_k(N+1) - q_k(N) (Index \text{ for a nucleophilic attacks}) (10)$$
$$f_k^-(k) = q_k(N) - q_k(N-1) (Index \text{ for elecrophilic attack}) (11)$$

Here, all symbols have their usual meaning[50,51]. Recently, another descriptor was introduced, which is a second order FF, also called as "dual descriptor" [50,53]. Dual descriptor is used to give a simple and instinctive way to chemical reactivity (Eq.  $(\underline{12})$ )

$$f^{2}(r) \approx f^{+}(r) - f^{-}(r)$$
 (12)

:

It was pointed out that [52,53], the electron acceptor regions are indicated by  $f^2(r) > 0$ , whereas, the electron donors regions are indicated by  $f^2(r) < 0$ . For better meta-inhibitor interactions both the regions should be aligned together.

The local softness is defined as the product of the global softness and the condensed FFs as shown below in Eq.  $(\underline{13})$ :

$$s_k^{\pm}(r) = S \times f_k^{\pm}(r)$$
(13)

The calculated Fukui indices and local softness, as well as the dual descriptor (second order Fukui indices) for the inhibitor molecule under probe are summarized in Table 5.The natural atomic charges of the neutral, anion and cation species of the neutral AA2 inhibitor are presented in Table SI4of the electronic supplementary material. The optimized structure of the neutral AA2 with the numbering systems for Fukui indices

is shown in Figure SI5of the electronic supplementary materials. It can be seen that the investigated inhibitor possesses the highest values of  $f_k^+$  which are located on the atoms of the aromatic rings (C13, C2, C12, C3, C4, C16, C14 andC6 indicating that these sites are electron acceptors. These results agree with the electron density distribution over the LUMO surface whereas N22, N21, O35, C6, C14, C1, C11, C4 and C16act as electron donor. Furthermore, as displayed in Table 5 and Figure 11a, the dual descriptor index ( $f^2(r)$ ) displays that the locations for the highest electron acceptor regions are follow the next pattern: C13 > C2 > C12 > C3 > C16 > C4 > C14, which indicated by  $f^2(r) > 0$ . On the other hand, the atoms that have the highest electron donating regions are arranged in the following trend: N22 > N21 > O35 > C1 > C11 > C8, which are indicated by the  $f^2(r) < 0$ . Thus the preferred site for the accepting electron was found on N22, N21 and O35, respectively.

### 4.3. Quantum chemical calculations of the protonated form of inhibitor molecule

It is worth to demonstrate how molecular property of the protonated form of the AA2 molecule play important role for the adsorption on the Fe(110) surface. When the AA2 molecule dissolves in acidic solution, the epoxy group (oxirane ring) is opened and converted into glycol. The optimized geometric configurations and the electrostatic potential map (ESP) of the CDR molecule are also shown in Figure 9. The HOMO and LUMO, as well their energies and the energy gap between them are also presented in Figure 10. The above mentioned global descriptors for the protonated form obtained from DFT calculation are also summarized in Table 4. Careful inspection of Table 4 and Figure 10 shows that the value of  $E_{\text{HOMO}}$  of the protonated form is shifted towards the less negative value in comparison to the  $E_{\text{HOMO}}$  value of neutral form. These results affirm that the protonated form has a higher tendency to donate the electrons than the neutral form, which is also supported by the value of  $\Delta N_{110}$ . Our results show that the  $\Delta N_{110}$  of the protonated form is 0.006 lower than that of the neutral form. On the contrary,  $E_{LUMO}$  value tabulated in Table 4 also shifted towards the less negative value compared with that of the neutral form, which affirms that the  $E_{LUMO}$  of the protonated form is larger than that of the neutral one. It is pointing out that electron acceptance capability in the protonated form is decreased, and the capability to back-donation interactions is reduced. Our results show that the electronegativity of the protonated form is 0.053 eV much lower than

that of the neutral one. Analysis of the energy gap values tabulated in Table 4indicates that the energy gap of the neutral species is lower than that of the protonated ones, which indicates that chemical reactivity of the neutral species is higher than that of the protonated form. Finally, the tabulated results (Table 4) shows that the dipole moment of the protonated inhibitor is much higher than that of the neutral species, reflecting that the dipole-dipole interactions between the protonated inhibitor and the metal surface is much stronger compared with that between the neutral inhibitor and the metal surface, however, it is important to mention that there isn't a clear relationship between the inhibition efficiency and the dipole moments. Thus the inhibition efficiency of the protonated form is higher than that of the neutral one. Analysis of the results showed neutral form of AA2 acts as better donor and protonated form of AA2 behaves as better acceptor.

### 4.4. Active sites analysis of protonated form of molecule

The Fukui functions  $(f_k^+ \text{and } f_k^-)$ , local softness  $(s_k^\pm(r))$  and dual descriptor  $(f^2(r))$  are also summarized in Table 5 and graphically shown in Figure 11b. The natural atomic charges of the neutral, anionic and cationic species of the protonated AA2 inhibitor are presented in Table SI4 of the electronic supplementary material. The optimized structure of the protonated AA2 with the numbering systems for Fukui indices is shown in Figure SI6of the electronic supplementary materials. According to Table 5 and Figure 11b the C2, C6, C4, C3, C12, C16, C14 and C13 atoms of the protonated form of the inhibitor molecule having high value of  $f_k^+$ , and therefore are exposed to accept electrons, while, N22, N21, O23, C1, C16, C11, C6, C4, C14 and C49 atoms having high value of  $f_k^-$  are suspected to transfer their electrons to the surface of the metal. Therefore, it is shown that in both case, the donor and the accepted centers of the electron to the meta surface of to the inhibitor molecule, respectively, are similar, which is totally agree with the electron density distribution over the HOMO and LUMO surfaces.

### 5. Molecular dynamics simulation

To get further information about the interaction between the AA2 molecules and the iron surface, molecular dynamics (MD) simulation was performed. As mentioned above, AA2 has a great tendency to occur ring-opening reaction under acidic solution. Thus, the ring open product was used for the simulation. The dynamics process was carried out and the whole system reached equilibrium until both temperature and energy of the system were balance.

The equilibrium configurations (top and side view) of AA2 adsorbed on the Fe(110) surface are shown in Figure (12a). It can be seen that the inhibitor molecule adsorb on the metal surface through the N, O atoms as well as the aromatic rings. The adsorption energy ( $E_{ads}$ ) for inhibitor adsorption can be calculated as following Eq. (14):

$$E_{ads} = E_{total} - (E_{surf+water} + E_{inh+surf}) + E_{water}$$
(14)

The symbols have their typical meaning. The adsorption energies in the present work were calculated from the average adsorption energy of the obtained equilibrium configurations.

### 6. Comparative efficiency

Literature study reveals that few of the tetra-functional macromolecular epoxy resins based organic inhibitors have been evaluated for their anti-corrosive behavior for steel in 1 M HCl media [7-9, 54]. Inhibition effectiveness of some common representatives of the similar inhibitors is presented in Table <u>6</u>.

It can be seen that these types of compounds are acted as good corrosion inhibitors and their compounds containing two aromatic rings and heteroatoms (N, O, S and P).

#### 6. Conclusions

From above experimental and theoretical studies, it can be concluded that:

- 1. The highest inhibition efficiency value for AA2 at  $10^{-3}$  M (optimum concentration) is 91.3 %.
- 2. The PDP results show that AA2 behaves a cathodic type of corrosion inhibitor.
- 3. The EIS results suggested that, AA2 protect the carbon steel form corrosion by the formation of a protective film at the metal surface.
- 4. Adsorption of the tested organic aromatic based multifunctional epoxy prepolymer molecules obeys Langmuir adsorption isotherm.
- 5. The  $\Delta G_{ads}$  value for AA2 is superior to -40 kJ/mol, indicating strongly interaction of AA2 onto the metallic surface.

- 6. Global quantum descriptors of the neutral and protonated species of the AA2 inhibitor molecule in aqueous solution concluded that the title molecule behaves as a good inhibitor for the carbon steel surfaces and it may be physically adsorbed by stacking on carbon steel.
- 7. The negative values of  $E_{ads}$  for AA2 at different temprature suggests a stronger adsorption strength between an AA2 molecule and metal surface.

#### **Conflicts of interest**

There are no conflicts to declare.

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Solution

### Tables

Table 1 Potentiodynamic polarization parameters for carbon steel corrosion in 1 M
HCl solution in the absence and presence of different concentrations of AA2.

Inh	<i>C</i> (M)	$E_{\rm corr}$	icorr	$\beta_{\rm a}$ (mV/dec)	-β <sub>c</sub>	η%
		( <b>mV</b> )	$(\mu A/cm^2)$		(mV/dec)	
Blank	-	-473.80	916.6(±1.78)	163.6(±1.12)	155(±1.63)	-
	$10^{-3}$	-482.52	81.66(±0.85)	91.5(±0.93)	177.9(±1.66)	91.0
AA2	10 <sup>-4</sup>	-500.71	94.29(±0.91)	89.4(±0.81)	135.7(±0.95)	89.7
	$10^{-5}$	-498.75	126.25(±1.05)	79.9(±0.74)	122.3(±0.81)	86.2
	$10^{-6}$	-419.37	227.22(±1.26)	83.9(±0.66)	122.2(±0.82)	75.2

**Table 2** Electrochemical impedance spectroscopy parameters for carbon steel

 corrosion in 1 M HCl solution in the absence and presence of different concentrations

 of AA2.

Inh	<i>C</i> (M)	$R_{\rm s} \left( \Omega. \rm cm^2 \right)$	$R_{\rm p} \left( \Omega. {\rm cm}^2 \right)$	$C_{\rm dl}~({\rm mF/cm}^2)$	η%	$\chi^2$
Blank	-	2.15(±0.03)	25(±1.03)	4.6(±0.08)	-	0.056
	10-3	1.56(±0.01)	290.1(±1.16)	0.077(±0.02)	91.3	0.104
AA2	$10^{-4}$	1.20(±0.01)	218.0(±1.03)	0.095(±0.01)	88.5	0.220
	10-5	1.18(±0.02)	189.9(±0.93)	0.111 (±0.01)	86.8	0.152
	10-6	0.99(±0.01)	098.0(±0.56)	0.125(±0.03)	74.5	0.210

**Table 3** The influence of temperature on the electrochemical parameters for carbon steel in 1M HCl and  $10^{-3}$  M of AA2.

<b>T</b> ( <b>K</b> )	m	E <sub>corr</sub> V/SCE	ļ	E <sub>ct</sub> %	
	Blank 10 <sup>-3</sup> M of AA2		Blank	10 <sup>-3</sup> M of AA2	-
298	- 473	-482	916	81.66	91
308	- 459	-496	1390	142.75	89
318	- 455	-488	2700	449.77	83
328	- 453	-511	4100	806.08	80

Theoretical parameters	Neutral inhibitor	Protonated inhibitor
Energy (hartree)	-1381.031808	-1722.829448
$E_{\rm HOMO}(\rm eV)$	-5.1827	-5.1607
$E_{\rm LUMO}({\rm eV})$	-0.777	-0.693
Ionization energy (I) (eV)	5.183	5.161
Electron affinity (A) (eV)	0.777	0.693
Energy gap, $\Delta E$ , (eV)	4.405	4.467
Global Electronegativity, χ (eV)	2.980	2.927
Global hardness, η (eV)	2.203	2.234
Global softness, S (eV <sup>-1</sup> )	0.454	0.448
Global electrophilicity, w (eV)	2.016	1.918
Global nucleophilicity, $\varepsilon$ (eV <sup>-1</sup> )	0.496	0.521
Number of transferred electrons, $\Delta N110$	0.4177	0.4237
Initial molecule-metal interaction energy, $\Delta \psi$ (eV),	1.8341	1.8567
Charge transfer model for donation and back- donation of charges, $\Delta E_{b,d}(eV)$	-0.551	-0.558
Electrodonating power $(\omega)$	3.781326584	3.660511171
Eelctroaccepting power, $(\omega^+)$	0.80124821	0.733495417
Net electrophilicity, $(\Delta \omega^{\pm})$	4.583	4.394
Dipole moment (Debye)	0.803	8.536

**Table 4** Calculated quantum chemical parameters of studied neutral and protonated forms of the inhibitor molecule.

 $\begin{aligned} \Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}, \ I = -E_{\text{HOMO}}, \ A = -E_{\text{LUMO}}, \ \pi = -\chi = 0.5(I+A), \ \eta = 0.5(I-A), \ S = 1/\eta, \ \omega = \chi^2/2\eta, \\ \varepsilon = 1/\omega, \ \Delta N_{110} = (4.82 - \chi_{\text{inh}})/2(\eta_{\text{inh}} + \eta_{\text{Fe}}), \ \Delta \psi = (\chi_{\text{Fe}} - \chi_{\text{inh}})^2/4(\eta_{\text{Fe}} + \eta_{\text{inh}}), \ \Delta E_{d-b} = -\eta/4, \ \omega^- = (3I+A)^2/16(I-A), \ \omega^+ = ((I+3A))^2/16(I-A), \ \Delta \omega^{\pm} = \omega^+ + \omega^- \end{aligned}$ 

	Neutral inhibitor							Protonated	inhibitor		
	$f_k^+$	$f_k^-$	$S_k^+$	$S_k^-$	$f^2(r)$		$f_k^+$	$f_k^-$	$S_k^+$	$S_k^-$	$f^2(r)$
C1	-0.00362	0.04884	0.00031	0.02217	-0.05246	C1	-0.01965	0.06665	0.00170	0.03026	-0.08630
C2	0.09954	0.02135	-0.00859	0.00969	0.07819	C2	0.10993	0.02685	-0.00949	0.01219	0.08308
C3	0.09473	0.02309	-0.00818	0.01048	0.07164	C3	0.09495	0.02472	-0.00819	0.01122	0.07023
C4	0.08953	0.03830	-0.00773	0.01739	0.05123	C4	0.09603	0.04613	-0.00829	0.02094	0.04990
C6	0.08945	0.04889	-0.00772	0.02220	0.04056	C6	0.10711	0.04649	-0.00924	0.02111	0.06062
C8	0.00099	0.02917	-0.00009	0.01324	-0.02818	C8	0.00762	0.02782	-0.00066	0.01263	-0.02020
C11	-0.00362	0.04880	0.00031	0.02216	-0.05242	C11	-0.02358	0.04762	0.00203	0.02162	-0.07120
C12	0.09474	0.02308	-0.00818	0.01048	0.07166	C12	0.07778	0.01568	-0.00671	0.00712	0.06210
C13	0.09955	0.02134	-0.00859	0.00969	0.07821	C13	0.07166	0.01715	-0.00618	0.00779	0.05451
C14	0.08946	0.04888	-0.00772	0.02219	0.04058	C14	0.07368	0.03447	-0.00636	0.01565	0.03921
C16	0.08952	0.03828	-0.00773	0.01738	0.05124	C16	0.07432	0.04781	-0.00641	0.02171	0.02651
C18	0.00099	0.02916	-0.00009	0.01324	-0.02817	C18	0.00848	0.01859	-0.00073	0.00844	-0.01011
N21	0.00836	0.10736	-0.00072	0.04874	-0.09900	N21	-0.02417	0.12333	0.00209	0.05599	-0.14750
N22	0.00836	0.10741	-0.00072	0.04876	-0.09905	N22	-0.02591	0.15067	0.00224	0.06840	-0.17658
C23	-0.00333	-0.01272	0.00029	-0.00577	0.00939	O23	0.00728	0.07369	-0.00063	0.03346	-0.06641
C26	-0.00351	-0.01275	0.00030	-0.00579	0.00924	C24	0.00896	-0.02047	-0.00077	-0.00929	0.02943
C29	-0.00334	-0.01273	0.00029	-0.00578	0.00939	C25	-0.03331	0.03274	0.00287	0.01486	-0.06605
C32	-0.00351	-0.01276	0.00030	-0.00579	0.00925	C26	0.01710	0.00775	-0.00148	0.00352	0.00935
035	0.02004	0.07296	-0.00173	0.03312	-0.05292	C28	-0.01241	0.01213	0.00107	0.00551	-0.02454
C36	-0.00147	-0.00186	0.00013	-0.00084	0.00039	C32	0.00641	-0.02660	-0.00055	-0.01208	0.03301
C37	0.00045	0.00283	-0.00004	0.00128	-0.00238	C33	-0.03201	0.03271	0.00276	0.01485	-0.06472
O38	0.00520	0.01067	-0.00045	0.00484	-0.00547	C36	-0.01010	0.00928	0.00087	0.00421	-0.01938
C42	-0.00152	-0.00192	0.00013	-0.00087	0.00040	C40	0.00777	-0.02371	-0.00067	-0.01076	0.03148
C43	0.00036	0.00268	-0.00003	0.00122	-0.00232	C41	-0.03095	0.03092	0.00267	0.01404	-0.06187
O44	0.00530	0.01074	-0.00046	0.00488	-0.00544	C44	-0.01291	0.01223	0.00111	0.00555	-0.02514
C48	-0.00147	-0.00186	0.00013	-0.00084	0.00039	C48	0.00879	-0.02130	-0.00076	-0.00967	0.03009
C49	0.00044	0.00284	-0.00004	0.00129	-0.00240	C49	-0.03346	0.03284	0.00289	0.01491	-0.06630
O50	0.00520	0.01067	-0.00045	0.00484	-0.00547	C52	-0.01227	0.01216	0.00106	0.00552	-0.02443
C54	-0.00152	-0.00192	0.00013	-0.00087	0.00040	056	-0.02345	0.02560	0.00202	0.01162	-0.04905
055	0.00036	0.00268	-0.00003	0.00122	-0.00232	058	-0.02103	0.01915	0.00181	0.00869	-0.04018
056	0.00530	0.010/4	-0.00046	0.00488	-0.00544	060	-0.02339	0.02554	0.00202	0.01160	-0.04893
						062	-0.02062	0.01915	0.00178	0.00869	-0.03977
						064	-0.01393	0.02463	0.00120	0.01118	-0.03856
						066	-0.025/0	0.02894	0.00222	0.01314	-0.05464
						068	-0.017/97	0.02039	0.00155	0.00926	-0.03836
						070	-0.02270	0.02557	0.00196	0.01161	-0.04827

**Table 5** Fukui functions analysis for both neutral and protonated species.

Type of corrosion inhibitor	Type of	С	Type of	$\eta_{Max}$	Ref
	solution	<b>(M)</b>	substrate	(%)	
Triglycidyl ether of triethoxy triazine	1M HCl	10-3	Carbon steel	88.0	[ <u>7</u> ]
S, S'-diglycidyl O, O'- dicarbonodithioate of	1M HCl	$10^{-3}$	Carbon steel	96.0	[ <u>7</u> ]
bisphenol A					
Octaglycidylether tetra-aniline para	1M HCl	$10^{-3}$	Carbon steel	98.0	[7]
methylene dianiline					
$\overline{N^1, N^1, N^2, N^2}$ -tetrakis (oxiran-2-ylmethyl)	1M HCl	10-3	Carbon steel	91.7	[ <u>8</u> ]
benzene-1,2-diamine					
Tetraglycidyl-1,2-aminobenzamide.	1M HCl	10-3	Carbon steel	96.0	[ <u>9</u> ]
4-methyl-N <sup>1</sup> ,N <sup>1</sup> ,N <sup>2</sup> ,N <sup>2</sup> -tetrakis (oxiran-2-	1M HCl	10-3	Carbon steel	92.9	[ <u>54</u> ]
ylmethyl) benzene-1,2-diamine					

**Table 6:** Inhibition efficiency comparisons for some traditional corrosion inhibitors.

Figure



Figure 1:Schematic outline for the synthesis of AA2



Figure 2: Evolution of open circuit potential (OCP) versus time for carbon steel in 1 M HCl with different concentrations AA2 at 298 K



**Figure 3:** Potentiodynamic polarization curves for carbon steel corrosion in 1 M HCl solution in the absence and presence of different concentrations of AA2



Figure 4: Nyquist diagrams for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of AA2



Figure 5:Equivalent circuit used for the analysis of the EIS data.



Figure 6: Bode diagrams for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of AA2



**Figure 7:**SEM-EDS micrographs of low carbon steel after 12 h of immersion in 1 M HCl solution: without inhibitor (a) and with  $10^{-3}$  M of AA2 (b).



**Figure 8:** Potentiodynamic polarization curves of carbon steel in 1 M HCl solution in the presence of  $10^{-3}$  M of AA2 at different temperatures.



**Figure 9:**Optimized molecular structure and electrostatic potential map (ESP) of the inhibitor molecule in its neutral (a) and protonated form (b) using DFT/B3LYP/6-

31+G(d,p) in aqueous solution.



**Figure 10:**Frontier molecular orbitals (HOMO and LUMO) and their energy values, as well as the energy gap energy diagram of the inhibitor molecule in its neutral (a) and protonated form (b) using DFT/B3LYP/6-31+G(d,p) in aqueous solution.



**Figure 11:**Graphical representation of the second order Fukui function  $(f^2(\mathbf{r}))$  for selected atoms in the investigated inhibitors in its (a) neutral forma and (b) protonated form). The optimized structures of the inhibitor and its protonated form are superimposed in the figure.



Figure 12: (a) The equilibrium configuration of AA2 adsorbed on Fe(110) surface;(b) dependence of adsorption energy on the temperature for adsorbed AA2 molecule on Fe(110).

Conflict of interest statement

"I, **Dr. Chandrabhan Verma** (the Corresponding Author), on behalf of other authors declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. There is also no conflict of interest in any way. I understand that the Corresponding Author is the sole contact for the Editorial process and is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs.

Dr. C. Verma On the behalf of all co-author NWU, Mafikeng South Africa

### **Highlights**

- An aromatic macromolecule (AA2) was synthesized and tested as inhibitor.
- Inhibition effect of AA2 was studied experimental and computational methods.
- > The macromolecule showed highest efficiency of 91.3% at  $10^{-3}$ M.
- The PDP results show that AA2 behaves as predominantly cathodic type of inhibitor.
- > AA2 forms surface protective films and protects from corrosion.