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Corrosion inhibition of mild steel in hydrochloric acid solution by an isatin-aniline compound

Abstract- *Recently the researchers go to the eco-friendly corrosion inhibitors. In the present investigation, isatin which found in many plants, Isatis tinctoria, Calanthe discolor and Couroupita guianensis has been used as corrosion inhibitor. An isatin-aniline compound, namely ethyl 4-amino-N-(3-isatinyl) benzoate (AIB), was successfully synthesized in high yield and its inhibition impact on corrosion of MS (mild steel) in hydrochloric acid as corrosive solution was examined via weight loss and Scanning electron microscope techniques. The results acquired appeared that AIB has employ perfect as a corrosion inhibitor at low concentrations towards mild steel in HCl bath. The impact of temperature on the corrosion behavior of MS in corrosive bath with presence of (250) ppm of AIB has been investigated in the range of temperatures (303-333) K. The thermodynamic parameters for inhibiting process were investigated to find out the mechanism of corrosion inhibition of MS acid bath.*

Keywords- *Corrosion inhibitor; Hydrochloric acid; Mild steel; SEM; thermodynamic parameters*

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1. Intreoduction

Among the various techniques of corrosion protection, the utilization of corrosion inhibitors was quite common. Corrosion inhibitor could be defined as substance that added in slight concentration to acidic or basic solution to decrease or block the interaction of the metal with the corrosive media [1]. The Inhibitors have been appended to cooling system, refinery unit, chemicals and/or oil and/or gas unit, boilers and so on. An excellent corrosion inhibitor may have heteroatoms in their chemical structures such as O, N, and S in addition to double and/or triple bonds through adsorption on the mils steel surface [2-5]. Numerous organic molecules nitrogen, oxygen and/or sulfur heterocyclic molecules are quite published as corrosion inhibitors of mild steel in acidic bath [6–9]. However, several of organic molecules were expensive and not easily denaturation. As a very soluble, active, cheap and eco-friendly organic molecule, isatin have been informed to synthesize the efficient corrosion inhibitors for metal surfaces [10–13]. The special tautomer of imine–amine and/or keto-enol with electronegative atoms N and O in addition to heterocyclic conjugate system, benefit the isatin-aniline molecules to adsorb on mild steel surface. The planarity (p) and lines pairs of electrons presents on N, O and S atoms are the important structural features that's controls the adsorption of these molecules onto the surface of the metal. The importance of this work lies in attesting the already established results on the corrosions inhibitions effects of various Schiff's bases on mild steel in acidic solutions [14-16]. The presents investigation aiming to study the corrosion inhibition impact of ethyl 4-amino-N-(3-isatinyl)benzoate (AIB) and its protective performance for mild steel in acidic solution by using of weight loss method, scanning electron microscopy technique, Moreover the and quantum chemical calculation was also studied, to understand the mechanism of inhibition.

2. Distribution System Reliability Evaluation

Chemicals materials have been purchased from Sigma-Aldrich The purity were investigated for the purchased compounds by Thin Layer Chromatography technique. Infrared spectrum for ethyl 4-((2-oxoindolin-3-ylidene) amino) benzoate was done by instrument "Thermo Scientific, NICOLET 6700 FTIR spectrometer". Ethyl 4-((2-oxoindolin-3-ylidene) amino) benzoate was also characterized by Nuclear magnetic resonance that was done by JEOL JNM-ECP 400 instrument.

I.Synthesis of the inhibitor (ethyl 4-amino-N-(3-isatinyl)benzoate (AIB).

A mixture of isatin and ethyl 4-aminobenzoate in 1:1 molar ratio were stirred well and refluxed in (30 mL) of methyl alcohol with few drops of glacial acetic acid for 6hrs.

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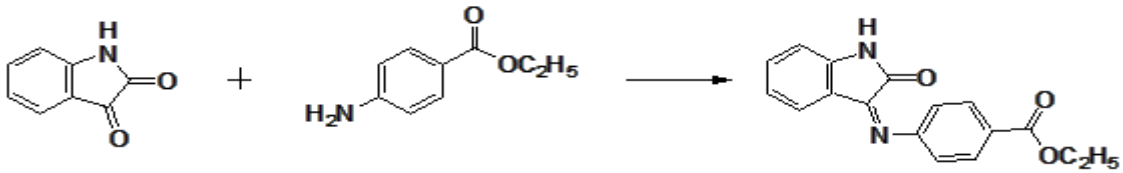

Figure 1. Chemical structure of AIB

The reaction mixture was cooled, and the precipitate was filtered washed repeatedly recrystallized from chloroform. Yield is 69%, melting point 183ºC. AIB was characterized by Fourier transforms infrareds (FTIRs) and ^{1}HNMR spectroscopy in addition to elemental analysis and purity of the AIB was checked by TLC. The molecular structure of AIB is given in Figure 1. FT-IR: 3205 (N-H str.), 2977 (CH aliphatic str.), 1603 (C=N str.), 1742 (-C=O str.), 1267 and 1059 (asy and sy C-O). ^{1}H NMR (δ ppm, DMSO-d6); 8.53 (s, 1H, NH), 7.11-7.90 (m, Ar-H), 4.31 (dd, 2H, CH2), 1.48(t, 3H, CH3).

3.Weight loss measurements

The coupons for the weight loss measurements were supplied from "Metal-Samples-Company" (St. Marys, PA, United States). The mild steel weight composition% were: Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Mn, 0.05; and Al, 0.01. The size was (3 cm × 3 cm × 0.1 cm). The coupons have been cleaned utilizing the chemical cleaning technique that recorded in [17]. Experiments have been performed in corrosive solution of 1 M hydrochloric acid bath having various AIB concentrations. Inhibition efficiency (η) has been calculated (equation 1) for inhibitor concentration 0, 50, 100, 150, 200 and 250 ppm for 3, 6 and 9 hrs.

$$\eta(\%) = [(W - W_i)/W] \times 100 \quad \ldots 1$$

where W and Wi are the weight loss in the absence and presence of an inhibitor respectively.

To evaluate the corrosion rate (ρ) we were used equation 2.

$$\rho(mpy) = 534W/dat \quad \ldots 2$$

where d, a and t were density of the coupon in g/cm3), area of the coupon in cm2 and exposure time in hours respectively.

4. Quantum chemical controls

Quantum chemical controls had performed to demonstrate the relation of structure of the AIB molecule as investigated inhibitor and the structure inhibition impact of AIB. The optimized structure of AIB was investigated regarding calculation done through DFT (density function theory) with basis set 6-31G.

HOMO (highest occupied molecular orbital energy), LUMO (lowest unoccupied molecular orbital energy) and μ (dipole moment) have been estimated to figuration the mechanism of inhibition. Regarding to reference [18], HOMO and LUMO for AIB as inhibitor is related to the ionization potential, I, and the electron affinity and also the electronegativity (χ), hardness (η) and softness (σ) were calculated.

5. Results and discussions

Synthesis

To synthesizes of AIB molecules as a corrosions inhibitors, the reactions sequence outlined in Figure 1. It was followed, starting from commercially available eco-friendly compound namely isatin that reacted with ethyl 4-aminobenzoate to form the target compound as a Schiff base compound. Synthesis of AIB has been done through refluxing of the eco-friendly compound isatin with ethyl 4-aminobenzoate with few drops of acetic acid, as catalyst followed by recrystallization. The AIB molecular weight was 294, that calculated regarding to the molecular formula (C17H14N2O3) and supported by elemental analysis (CHN) technique. AIB could dissolved in the solvents namely "acetone, dichloro methane ,dimethyl formamide, dimethylsulfoxide". Spectrum of FT-IR for AIB appear the bands 3205cm−1 for lactam, 2977for C-H aliphatic and C=O stretching at 1742 cm−1. The bands at 1603, cm−1 are for C=N azomthane, also the bands at 1267 and 1059 were for asymmetric and symmetric C-O respectively. The 1H-NMR spectrum exhibits a singlet at δ8.53 ppm due to the NH proton and at δ 8.50 (s, 1H, for −NH) and δ 7.11-7.90 (m, for Aromatic rings). The signals at 4.31ppm were dd for 2H of methylene group and 1.48ppm as t, 3H, for methyl group.

6.Weight loss study

I. Effect of concentration

An AIB molecule as inhibitor has been investigated for 3, 6 and 9 hrs. Of for various concentrations and the data for weight loss technique has been displayed in Figure 2. The highest inhibition efficiency for AIB as corrosion inhibitor reaches to 80% for the highest employed concentration. Moreover, the inhibition efficiency for AIB was increases with increasing concentration as shown in Figure 2.

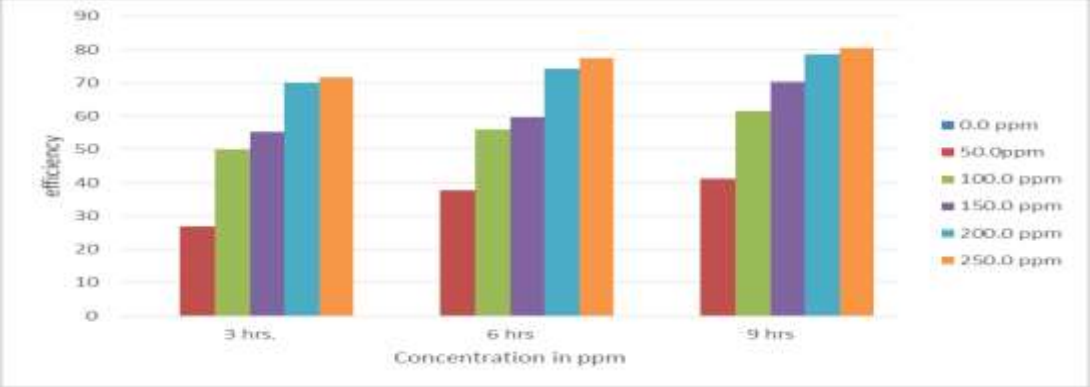

Figure 2. Inhibitionsefficiencies of mildssteel in 1 M HCl in the absences and/or presence of AIB.

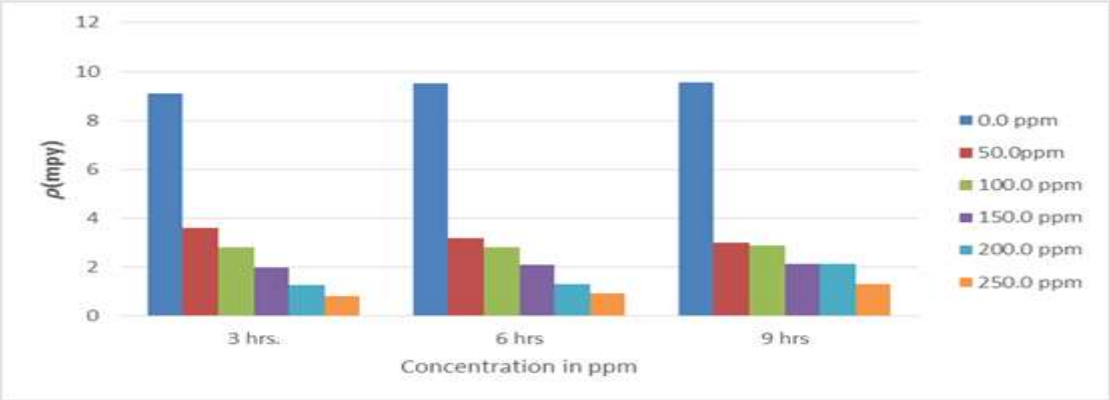

Figure 3. Corrosion rate of mild steel in 1 M HCl in the absence and/or presence of AIB.

Corrosion rate has been evaluated for various concentrations of AIB for the duration 3, 6 and 9 hrs, at 303 K are shown in Figure 3. It can be sown from Figure 3, that AIB diminutive the corrosion in HCl solutions for mild steel.

II.Effect of temperature

Temperatures range of 303 to 333 K impact for 9hrs on the efficiencies for corrosion inhibition of AIB for mild steel in corrosive solution has been studied by weight loss technique in absence and/or presence of AIB are shown in Figure 4.

Figure 4 displayed the values of inhibition efficiencies at various temperatures. It can be shown that the inhibition efficiencies decrease with increase in temperatures and the lowest inhibition efficiency at the highest investigated temperature that was 333 K, and this may due to dissociation of coated film on mild steel surface that form from the interaction of AIB molecule with metal surface and this coated film is responsible for corrosion.

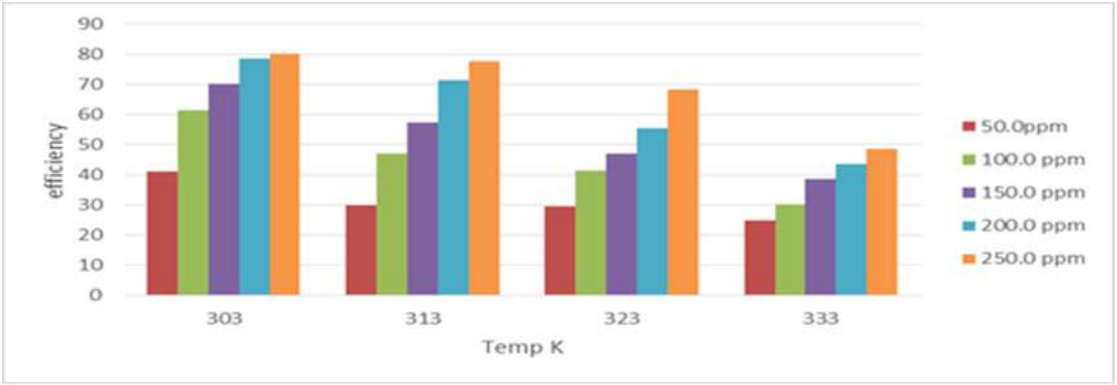

Figure 4. Inhibition efficiency in the presence of AIB at different temperatures for 9hrs.

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7.Theoretical calculations

Theoretical calculations that acquired from the Density functional theory were displayed in Figure 5.Quantums chemical parameters [highest occupied molecular orbitals (EHOMO), energy of lowest unoccupied molecular orbitals (ELUMO), energy gap (DE), dipole moments (l), electronegativity (v), electron affinity (A), global hardness (g), softness (r) and ionization potentials (I)] which were responsible for the inhibition efficiencies for AIB as corrosion inhibitor were showed in Table 1. EHOMO is predominating linked with the ability for donating electrons and hence the molecules which have high value of HOMO were probable reference a tendencies of the molecules for donating electrons to suitable acceptors that have unequipped molecular orbital. At the same time LUMO refer to the capability for accepting electrons [19]. For these facts if LUMO energy is low this probable refers to accepting electrons and high inhibition efficiency. Moreover, if the HOMO energy is high that led to ability of AIB molecules as inhibitor to bending with surface of mild steel and the increases inhibition efficiency. So AIB molecules that were calculated displayed that the highest HOMO level at -9.453 eV and the lowest LUMO level at -4.603eV. This may demonstrate that the highest inhibition efficiency of AIB is due to the increasing HOMO energy and decreasing LUMO energy. This agreement with the experimental observations proposing that AIB has the 80% as highest inhibition efficiency. From Figure 5 it can be shown that the HOMO of AIB density was distributed over the benzene ring (for aniline) and also the five-member ring with isomethane group. The LUMO density is localized on the isatin and C=N group. Inhibition of corrosion is generally explained by adsorption of AIB inhibitor molecules onto the surface of mild steel. Physical adsorption different from chemical adsorption in interactions between the AIB molecules as inhibitor and metal surface. The physical one of electrically charged but the chemical adsorption imply transfer electrons from the inhibitor molecule to the unequipped molecular orbitals of the metal. The impact of temperature on the inhibition efficacies of AIB and adsorption parameters showed that physical adsorption phenomenon would be acceptable [20]. In our investigation, AIB displayed perfect inhibition impact versus the corrosion of surface of mild steel in corrosive solution. The results displayed that the AIB molecules as corrosion inhibitor have higher energy gap 4.85eV. This parameter supplies stability measurement for the complex formation of AIB molecules and mild steel surface. Also, dipole moment of the AIB molecules as corrosion inhibitors represent the extreme exceedingly employed parameter for polarity description [21]. Dipole moment defined as the fruit of charge on the atom and the atoms bond distance. The dipole moment, is the mirror, of a molecule global polarity. The DFT investigation show that the dipole moment correlated with the corrosion inhibition efficiency and also the increasing of dipole moment led to higher inhibition efficiency. Higher ionization energy referred to higher stability and the low value of ionization energy referred to high reactivity of the AIB molecules [22]. Ionization energy with low value that was -9.453 (eV) of AIB refer to high inhibition efficiency. Absolute hardness (η) and softness (σ) are significant characteristics to stability measurement and reactivity. The apparent characteristic was the chemical hardness principally signifies the resistance toward polarization of the electron cloud of molecules under little disturbance of chemical reaction. A hard molecules have considerable energy gap and a soft molecules have little energy gap [23]. Our results of AIB molecules as corrosion inhibitor with value of 7.028 eV. In general, the inhibitor with the least value of absolute hardness (that is highest value of absolute softness) is expected to have the highest inhibition efficiency [24]. AIB with the high softness value has the highest inhibition efficiency.

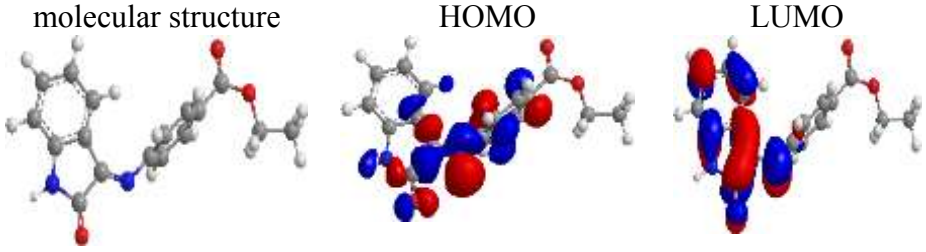

Figure 5. The molecular structure, HOMO and LUMO of the AIB as inhibitor.

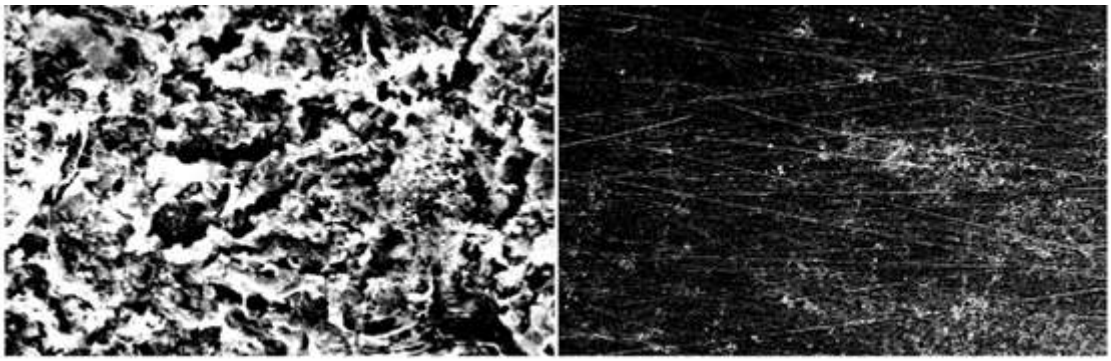

Figure 6. The SEM micrograph for mild steel in 1.0 M HCl.

8. Scanning electron microscopy.

SEM analysis was performed to investigate the mild steel morphology in absence and presence of highest investigated AIB molecules as corrosion inhibitor at 303K for 6 hrs in hydrochloric acid as corrosive solution as showed in Figure 6. It has been sown that corrosive solution without inhibitor due to the high decay average of surface of mild steel, where as thin film covered the mild steel surface in addition of AIB. The cracks that displayed in the protected layer may to dehydration of mild steel surface These results were evidences that AIB adsorb on surface of mild steel with isolating mild steel surface from the corrosive bath

Conclusions.

The results of this investigation revealed that the ethyl 4-amino-N-(3-isatinyl) benzoate (AIB) functioned as a good corrosion inhibitor for MS in HCl solution. The maximum inhibition efficiency of AIB at highest investigated concentration was up to 80%, but decreases with rising temperatures, that indicate physical adsorption. AIB represent an active inhibitor with good inhibitive impacts due to its structure that having nitrogen and oxygen atoms. SEM investigation support the formation of a protective film by AIB molecule on the surface of mild steel. The inhibition characterization of the AIB revealed there role in the protection of MS in HCl solution.

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