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3-Amino alkylated indoles as corrosion inhibitors for mild steel in 1M HCl: Experimental and theoretical studies



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ABSTRACT

The present study describes the influence of ring and ring size of three 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) on mild steel corrosion in 1M HCl solution using gravimetric, electrochemical, surface morphology (SEM, AFM), quantum chemical calculations and molecular dynamics simulations methods. Both experimental and theoretical results showed that the 3-amino alkylated indoles with cyclic amino groups exhibit higher inhibition efficiency compared to the one with opened-chain amino group. The results further suggested that the inhibition efficiency increases with increasing ring size of the amino group such that the piperidine-containing (6-membered ring) 3-amino alkylated indole showed higher inhibition performance than the pyrrolidine-containing (five membered) 3-amino alkylated indole. Experimental results revealed that the inhibition efficiency increases with increasing concentration of the inhibitors. Maximum inhibition efficiencies of 94.34% for AAI-1, 96.08% for AAI-2 and 96.95% for AAI-3 were obtained at 0.862 mM concentration. EIS measurements showed that the studied compounds inhibit mild steel corrosion by adsorbing on the steel surface. Polarization studies revealed that the compounds are cathodic type inhibitors. The adsorption of the studied compounds obeyed the Langmuir adsorption isotherm. SEM and AFM surface morphology analyses also provided evidence of formation of adsorbed film of the AAIs on the steel surface. Theoretical parameters such as E_{HOMO} and electronegativity derived from quantum chemical calculations as well as binding energy derived from molecular dynamics simulations studies adequately corroborate the trend of experimental inhibition efficiencies of the studied inhibitors.

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1. Introduction

Acid solutions are commonly used for pickling and also for the removal of rust and scales in petroleum industries [1-4]. The use of acid solutions for these industrial activities results in loss corrosion and eventually loss of metals. Addition of organic corrosion inhibitors, which are compounds that contain heteroatoms (e.g. N, O and S), double and triple bonds and aromatic rings has been identified as one of the most practical and economical ways of controlling metal corrosion [5-8]. These compounds inhibit metallic corrosion by becoming adsorbate at metal/electrolyte interfaces in which polar functional groups such $-NH_2$, -OH, -CN, $-NO_2$ etc. and pi-electrons of the double and triple bonds and aromatic rings act as adsorption centers [9-11]. Adsorption of these compounds depends upon several factors including molecular weight, nature of substituents, solution temperature, nature of inhibitor and electrolytes etc. [12,13]. However, most of the previously existing corrosion inhibitors are toxic and non-environmental friendly [14,15]. The current strict measures on environmental regulations and increasing ecological awareness have shifted the attentions of corrosion control experts toward the development of efficient and environmentally benign corrosion inhibitors [16–18]. In this direction, multicomponent reactions (MCRs), which combine three or more substrates is one of the most relevant current approaches that are able to produce several bonds in one step [19-22]. In addition, the MCRs have other several advantages including operational simplicity, facile automation and minimized waste generation, because of the reduction in the number of work-up, extraction and purification stages [19,23]. In spite of the theory of famous ancient philosopher of Greece, namely Aristotle, the "No Coopora nisi Fluida" which means "No reaction takes place in absence of solvent", in recent years organic synthesis in solid

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phase (solvent free condition) attracted great deal of attraction due to their reduce pollution, low costs, and simplicity in process and handling [24]. Certainly, in several cases, solvent free reactions takes place with high yield and selectivity than does their solution counterpart because of the more tight and regular arrangement of molecules in the crystal form [20,25]. Furthermore, "green chemistry" emphasizes the optimization of synthetic methodologies to reduce environmental pollution, cost and tedious work-ups. This new challenge has led to a growing interest in the field of organic synthesis using catalyst derived from natural resources [26,27]. In asymmetric organocatalysis, consumption of L-proline provides the means of upholding the essential principles of green chemistry as it is directly isolated from natural biological sources without use of any hazardous chemical and/or solvents such as DMSO, DMF and other chlorinated solvents [28]. Literature survey reveals that indole and its derivatives act as efficient metallic corrosion in different electrolytic media [29-33]. These compounds inhibit metallic corrosion by becoming adsorbate at the metal/electrolyte interface in which indole moiety acts as adsorption center.

In the present study, the effect of the type of amine (opened chain or cyclic) as well as ring size of cyclic amine on the corrosion inhibition efficiency of three newly synthesized 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) on mild steel corrosion in 1M HCl solution is being investigated for the first time. The corrosion inhibition performances of the three newly synthesized AAIs were determined using weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques. Quantum chemical calculations and molecular dynamics simulations studies were also carried out to provide more insights into the theoretical explanations of the inhibition activities of the studied compounds.

2. Experimental section

2.1. Materials

2.1.1. Electrode and reagents

The mild steel specimens for weight loss, electrochemical and surface measurements were cut form commercially available mild steel sheet having chemical composition (wt%): C (0.076), Mn (0.192), P (0.012), Si (0.026), Cr (0.050), Al (0.023), and Fe (balance). The exposed surface of the working electrodes were cleaned successively with emery papers of different grade (600, 800, 1000, and 1200), washed with deionized water, degreased with acetone, ultrasonically cleaned with ethanol and stored in moisture free desiccator before used in the experiments. Hydrochloric acid (HCl, 37%, MERCK) and double distilled water were used for preparation of test solution (1M HCl).

2.1.2. Inhibitors synthesis

3-amino alkylated indoles (AAIs) used in the present study were synthesized by the method described earlier [34]. In a typical experimental procedure, 1 mmol of the aldehyde, 1 mmol of the secondary amine, 1 mmol indole and 30 mol% of the L proline were placed in a round-bottom flask and stirred at room temperature. The progress and completion of the reaction was monitor by TLC method. After, completion of the reaction, the reaction mixtures were diluted with water and then extracted with ethyl acetate. The crude products were purified by column chromatography to give the corresponding inhibitors. Synthetic scheme of investigated inhibitors is given in Fig. 1 and chemical structures, abbreviations, IUPAC name and analytical data of the synthesized compounds are given in Table 1.

2.2. Methods

2.2.1. Weight loss measurements

Cleaned, dried and accurately weighted mild steel specimens having dimension 2.5 cm \times 2.0 cm \times 0.025 cm were immersed in 1M HCl without and with different concentrations of AAIs for 3 h. After elapsed time, these specimens were removed, washed with distilled water and acetone, dried in moisture free desiccator, and again weighed accurately. To ensure the reproducibility of the weight loss results, each experiment was triply performed and mean values are reported at each concentration. From the calculated weight loss, inhibition efficiency (η %) was derived using following relationship [35]:

$$\eta\% = \frac{w_0 - w_i}{w_0} \times 100 \tag{1}$$

where w_0 and w_i are the weight loss values in the absence and presence of AAIs at different concentrations, respectively.

2.2.2. Electrochemical measurements

The mild steel specimens with exposed area 1 cm² (one sided) were utilized for all electrochemical measurements were performed under potentiodynamic condition using Gamry Potentiostat/Galvanostat (Model G-300) instrument. Gamry Echem Analyst 5.0 software installed in the computer was used to fit and analyzed all electrochemical data. The instrument consist of a mild steel working electrode (WE), platinum as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Before starting the electrochemical experiments, the working electrode were allowed to corrode freely for 30 min in order to attain steady open circuit potential (OCP). During polarization measurements, the cathodic and anodic Tafel slopes were recorded by changing the electrode potential from 0.25 to + 0.25 V vs corrosion potential (E_{corr}) at a constant sweep rate of 1.0 mV s⁻¹. The corrosion current density (i_{corr}) was calculated by extrapolating the linear segments



Fig. 1. Synthetic route of studied AAIs.

Table 1

IUPAC name, molecular structure, molecular formula, and analytical data of studied AAIs.



of Tafel slopes (cathodic and anodic). From the calculated i_{corr} value inhibition efficiency was calculated using following relation [35]:

$$\eta\% = \frac{i_{\rm corr}^0 - i_{\rm corr}^i}{i_{\rm corr}^0} \times 100 \tag{2}$$

where, i_{corr}^0 and i_{corr} are corrosion current in the absence and presence of AAIs, respectively.

Electrochemical impedance measurements were carried out at open circuit potential in the frequency range of 100 kHz to 0.01 Hz using AC signal of amplitude 10 mV peak to peak. The charge transfer resistances were calculated from Nyquist plots. The inhibition efficiency was calculated using following equation [35]:

$$\eta\% = \frac{R_{\rm ct}^{\rm i} - R_{\rm ct}^{\rm 0}}{R_{\rm ct}^{\rm i}} \times 100 \tag{3}$$

where, R_{ct}^0 and R_{ct}^i are charge transfer resistances in absence and presence of AAIs, respectively.

2.2.3. SEM, and AFM measurements

For surface analysis, the cleaned mild steel specimens of above mentioned composition were allowed to corrode for 3 h in absence and presence of optimum concentration of AAIs. Thereafter, the specimens were taken out washed with water, dried and employed for SEM and AFM analysis. The SEM model Ziess Evo 50 XVP was used to investigate the micromorphology of mild steel surface at $500 \times$ magnification. NT-MDT multimode AFM, Russia, 111 controlled by solvers canning probe microscope controller was employed for surface analysis by AFM method. The single beam cantilever having resonance frequency in the range of 240–255 kHz in semi contact mode with corresponding spring constant of 11.5 N/m with NOVA programme was used for image interpretation. The scanning area during AFM analysis was 5 mm \times 5 mm.

2.2.4. Quantum chemical calculations

Quantum chemical calculations were carried out on the investigated AAIs using the density functional theory (DFT) method involving the Becke three-parameter hybrid functional together with the Lee-Yang-Paar correlation functional (B3LYP) [36]. The 6-31 + G(d, p) basis set was chosen for all the calculations. The calculations were carried out with the aid of Gaussian 09 software for Windows (Revision D.01) [37]. The optimized geometries of the compounds were confirmed to correspond to their true energy minima by the absence of imaginary frequency in the computed vibrational frequencies. All quantum chemical parameters were derived based on the electronic parameters of the most stable conformers of the molecules. The frontier molecular orbital (FMO) energies, that is, the highest occupied molecular orbital energy (E_{HOMO}) and the lowest unoccupied molecular energy (E_{LUMO}) were calculated. Other parameters such as the energy gap (ΔE), global hardness (η), global electronegativity (χ), and the fraction of electrons transfer (ΔN) from the inhibitor to the metal atom were computed respectively according to the equations [40,41]:

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \tag{4}$$

$$\eta = \frac{1}{2} (E_{\text{LUMO}} - E_{\text{HOMO}}) \tag{5}$$

$$\chi = -\frac{1}{2}(E_{\rm LUMO} + E_{\rm HOMO}) \tag{6}$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$$
(7)

where χ_{Fe} and η_{inh} denote the electronegativity and hardness of iron and inhibitor, respectively. A value of 7 eV/mol was used for the χ_{Fe} , while η_{Fe} was taken as 0 eV/mol for bulk Fe atom in accordance with the Pearson's electronegativity scale [40]. The total energy change (ΔE_T) that accompanies the donor-acceptor charge transfer process was calculated according to the approximation made by Gomez et al. [41]:

$$\Delta E_T = \frac{-\eta}{4} \tag{8}$$

where η was approximated to the chemical hardness of the inhibitor molecule. Selected dihedral angles that might have some correlations with the experimental inhibition efficiency of the compounds were also reported.

2.2.5. Molecular dynamics simulations

Forcite module in the Material Studio Software 7.0 from BIOVIA-Accelrys, USA was adopted to carry out the quench molecular dynamics (MD) simulations. The simulation was carried out with Fe (110) crystal with a slab thickness of 5 Å. The Fe (110) plane was enlarged to a (10 × 10) supercell to provide a large surface for the interaction with the inhibitors. After that, a vacuum slab with 30 Å thicknesses was built above the Fe (110) plane. For the whole simulation procedure, the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field was used to optimize the structures of all components of the system of interest. The MD simulations were performed in NVT canonical ensemble at 298 K with a time step of 1.0 fs and a total simulation time of 500 ps using Anderson thermostat.

The interaction energy (E_{int}) of molecules with Fe surface was obtained using the following equation [42,43]:

$$E_{\rm int} = E_{\rm total} - (E_{\rm Fe\ surface} + E_{\rm molecule}) \tag{9}$$

where E_{total} is the total energy of the molecules and the metal surface system; E_{surface} is defined as the energy of metal surface without adsorption of molecules and E_{molecule} is the energy of isolated molecules. The binding energy is the negative of the interaction energy and is given as:

$$E_{\rm bin} = -E_{\rm int}.\tag{10}$$

3. Results and discussions

3.1. Weight loss experiments

3.1.1. Effect of AAIs concentration

Table 2 represents the parameters derived from the weight loss experiments after 3 h immersion time in absence and presence different concentrations of the investigated inhibitors. It can be seen from the results that inhibition efficiency increases with increasing concentration of all inhibitors and maximum values of inhibition efficiencies of 94.34% for AAI-1, 96.08% for AAI-2 and 96.95% for AAI-3 were obtained at 0.862 mM concentration. However, careful examination of the results depicted in Table 2 showed that very slight increase in the inhibition efficiency was observed on increasing inhibitors concentration from 0.689 mM to 0.862 mM suggesting that 0.689 mM is the optimum concentration. Increase in the inhibitors concentration resulted in the increased surface coverage which ultimately increases the inhibition efficiency. The higher inhibition efficiency of AAI-2 as compare to AAI-1 could be as a result of larger surface coverage by the pyrrolidine ring because of its ring structure present in AAI-2 as compare to its open chain structural analogues of AAI-1. While, the higher inhibition efficiency of AAI-3 as compare to AAI-2 can be explained on the basis of

Table 2

The weight loss parameters obtained for mild steel in 1M HCl containing different concentrations of AAIs.

Inhibitor	Conc (mM)	Weight loss (mg)	$C_{\rm R}$ (mg cm ⁻² h ⁻¹)	Surface coverage (θ)	η%
Blank	0.0	230	7.66	-	_
AAI-1	0.172	91	3.033	0.6043	60.43
	0.345	37	1.233	0.8391	83.91
	0.517	21	0.700	0.9086	90.86
	0.689	14	0.466	0.9391	93.91
	0.862	13	0.433	0.9434	94.34
AAI-2	0.172	68	2.266	0.7043	70.43
	0.345	28	0.933	0.8782	87.82
	0.517	16	0.533	0.9304	93.04
	0.689	10	0.333	0.9565	95.65
	0.862	9	0.300	0.9608	96.08
AAI-3	0.172	58	1.933	0.7478	74.78
	0.345	25	0.833	0.8913	89.13
	0.517	13	0.433	0.9434	94.34
	0.689	8	0.266	0.9652	96.52
	0.862	7	0.233	0.9695	96.95

size of the heterocyclic rings. AAI-3 possesses piperdine ring which has comparatively larger molecular size and cover the larger surface area as compare to pyrrolidine ring present in the AAI-2 [44,45]. From these results it can be concluded that inhibition efficiency of 3-amino alkylated indoles (AAIs) increases on introducing the ring in the inhibitor molecule as well as on increasing the ring size (or decreasing the ring strain). The increased inhibition efficiency of the AAIs, with introducing the ring and increasing the length of hydrophobic carbon/alkyl chain is attributed due to repulsion between the non-polar hydrophobic chain and the polar water phase, which in turn force the AAIs to adsorb at metal and electrolyte interfaces in order to decrease that repulsion [48,99]. Further, in presence of surface active molecules (inhibitors) in the solution cause distortion of the solvent liquids structure and thereby increase the free energy of the system. As a compromise, the AAIs concentrate at metal/electrolyte interfaces because there, the thermodynamic best arrangement was possible. The AAIs adsorb on the metal/ electrolyte interface in such a way that polar part of the molecules oriented toward metallic surface leaving the nonpolar hydrophobic alkyl part into the solution which repel the aqueous corrosion fluid and thereby inhibit corrosion [48-50].

3.1.2. Effect of solution temperature

In order to study the effect of temperature on the corrosion inhibition efficiency of 3-amino alkylated indoles on mild steel corrosion in 1M HCl, the weight loss experiments were performed in absence and presence of optimum concentrations of the studied inhibitors at different temperature ranging from 308 to 338 K. The values of corrosion rates (C_R) and percentage inhibition efficiency (η %) obtained at different temperature for studied inhibitors are given in the Table 3. It can be seen from the results that η % decreases and C_R increases with increasing the solution temperature. The increased C_R at elevated temperature might be attributed due to rapid etching, desorption and decomposition and/ or rearrangement of the inhibitors molecules [51]. The temperature dependency of C_R can be best represented by Arrhenius equation, where the natural logarithm of C_R is a linear function of 1/T [52]:

$$\log(C_R) = \frac{-E_a}{2.303RT} + \log A \tag{11}$$

where C_R is the corrosion rate in mg cm⁻² h⁻¹, E_a is the apparent activation energy, A is the Arrhenius pre-exponential factor, R is the gas constant and T is absolute temperature. The activation energy for metallic corrosion is the minimum amount of energy that is required in order to produce the corrosion products, such as rust and scales [7,53]. High values of E_a are generally associated with low corrosion rates while low values of E_a are associated with high corrosion rates. Fig. 2 represents the Arrhenius plots from the intercepts of which values of E_a are calculated. The calculated values of E_a were 76.072 kJ mol⁻¹, 80.461 kJ mol⁻¹ and 83.145 kJ mol⁻¹ for AAI-1, AAI-2 and AAI-3, respectively. These results showed that values of E_a are higher in presence of inhibitors as compare to in their absence (28.48 kJ mol⁻¹). The increased values of E_a in presence of AAIs suggest the physical adsorption that occurs during first stage of the adsorption processes. [54,55].

Table 3

Variation of $C_{\rm R}$ and η % with temperature in absence and presence of optimum concentration of AAIs in 1M HCl.

Temperature (K)	Corrosion rate ($C_{\rm R}$) (mg cm ⁻² h ⁻¹) and inhibition efficiency (η %)							
	Blank		AAI-1		AAI-2		AAI-3	
	C _R	η %	C _R	η %	C _R	η %	C _R	η %
308	7.66	-	0.46	93.99	0.33	95.69	0.26	96.60
318	11.0	-	1.30	88.81	1.00	90.90	0.80	92.72
328	14.3	-	3.10	78.32	2.46	82.79	1.93	86.50
338	18.6	-	6.50	65.05	5.43	70.80	4.86	73.87



Fig. 2. Arrhenius plots for the corrosion of mild steel in 1M HCl.

However, it is well known that the adsorption behavior of most of the organic inhibitors involve both physical as well as chemical processes [54,55]. Therefore, it is concluded that, the adsorption of these molecules on the mild steel surface from HCl solution takes place through both physical and chemical processes simultaneously with domination of physical one.

3.1.3. Adsorption isotherm

Adsorption isotherm provides the information about the nature of interaction between the inhibitor molecule and the metal surface and therefore it is one of the most important topics in the field of corrosion. The adsorption isotherm provides the structural information about double layer in addition to the thermodynamic information's. The adsorption may be chemisorption, physisorption or mixed type adsorption. In order to study the nature of adsorption of inhibitors undertaken in the present study on metallic surface, several isotherms such as Langmuir, Temkin and Frumkin etc. were tested. Nevertheless, the values of regression coefficient (R^2) showed the Langmuir isotherm gave the best fit as the numerical values of R^2 were close to unity for all studied inhibitors. According to the Langmuir isotherm, the degree of surface coverage (θ) is related to the inhibitor concentration (C) by following relation [56]:

$$K_{\rm ads}C = \frac{\theta}{1-\theta} \tag{12}$$

where K_{ads} is the equilibrium constant of the adsorption process, *C* is the molar concentration of AAIs and θ is the degree of surface coverage of AAIs at metallic surface. The values of surface coverage obtained at different concentrations of the AAIs from weight loss experiments were used to obtain the Langmuir adsorption isotherm plots (Fig. 3) which enabled the calculation of the values of K_{ads} . The K_{ads} related to the standard free energy of adsorption (ΔG^0_{ads}) by the following relation [57]:

$$\Delta G^{0}_{ads} = -RT \ln(55.5K_{ads}). \tag{13}$$

The numerical value 55.5 represents the molar concentration of water in acid solution. *R* is the gas constant and *T* is absolute temperature. The calculated values of K_{ads} and ΔG^0_{ads} are given in Table 4. High values of K_{ads} suggest that the adsorption of the AAIs on mild steel surface is easy and strong [58]. Previous, studies show that the value of ΔG^0_{ads} around -40 kJ mol⁻¹ or more negative is consisted with charge sharing between metal and inhibitor molecule (chemisorption) [59,60]. While the value of ΔG^0_{ads} around -20 kJ mol⁻¹ or less negative is consisted with electrostatic interaction between charged



Fig. 3. The values of K_{ads} and ΔG^0_{ads} derived from Langmuir adsorption isotherms for mild steel in 1M HCl in the presence of the studied AAIs at different temperatures.

inhibitor molecule and metallic surface (physisorption) [59,60]. Results depicted in Table 4 showed that values of ΔG^0_{ads} in the present study at different temperatures vary from -32.98 to -36.96 kJ mol⁻¹ suggesting that adsorption of the AAIs on mild steel surface is a combination of chemisorption and physisorption [61,62].

3.2. Electrochemical measurements

3.2.1. Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out in absence and presence of different concentrations of the investigated inhibitors in order to understand the process of anodic oxidative metallic dissolution and cathodic reductive hydrogen evolution. The potentiodynamic polarization curves for mild steel in absence and presence inhibitors are shown in Fig. 4. The values of potentiodynamic polarization parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes (β_a , β_c) were obtained from the polarization curves through extrapolation method and are included in Table 5. It can be seen from the results (Table 5 and Fig. 4) that presence of AAIs significantly reduced the values of corrosion current densities for both anodic and cathodic half reactions. This finding indicates that inhibitors undertaken in the present study successfully inhibited both anodic oxidative dissolution of mild steel and cathodic reductive evolution of hydrogen [63]. The decreased values of $i_{\rm corr}$ in presence of inhibitors are attributed due to blocking of the active centers present on the metallic surface [64]. It is obvious from the Fig. 4 that in presence of inhibitors the corrosion potential shifted toward more negative direction. Further, it can be observed from the results shown in Table 5 that values of β_c are more affected by inhibitors as compare to the values of β_a when compared to the values of β_a and β_c of free acid solution indicating that investigated inhibitors act as cathodic type inhibitors [65].

3.2.2. Electrochemical impedance spectroscopy (EIS) study

The influence of the investigated compounds on the corrosion behavior of mild steel in 1M HCl was also studied by EIS method in

able 4

The values of K_{ads} and ΔG^0_{ads} for mild steel in absence and presence of optimum concentration of AAIs in 1M HCl at different studied temperature.

Inhibitor	$K_{\rm ads} (10^4{ m M}^{-1})$				$-\Delta G^{0}_{ads}$ (k J mol ⁻¹)			
	308	318	328	338	308	318	328	338
AAI-1	1.85	0.89	0.43	0.22	35.45	34.68	33.80	32.98
AAI-2	2.63	1.11	0.54	0.29	36.36	35.27	34.40	33.72
AAI-3	3.32	1.52	0.76	0.34	36.96	36.10	35.36	34.15



Fig. 4. Polarization curves recorded for mild steel in the absence and presence of different concentrations of (a) AAI-1, (b) AAI-2, and (c) AAI-3.

order to support the results of weight loss and polarization studies. The Nyquist plots obtained from the EIS for mild steel in 1M HCl in without and with different concentrations of studied inhibitors is shown in Fig.5a. Inspection of the Fig.5a shows that the value of impedance modulus for uninhibited specimen was much smaller than that for inhibited specimen. Further, it is also observed that the impedance modulus gradually increases with increasing the concentration of the inhibitors. It is also obvious from It is obvious from Fig.5a that the Nyquist plot in absence of inhibitors shows a slightly depressed single semicircle capacitive loop and only one time constant was obtained in the Bode plots (single maxima in Bode plots). This finding suggests that corrosion of mild steel in acid solution in the absence of inhibitors is mainly controlled by charge transfer process [56,57]. In the Nyquist plots, the difference in real impedance at lower and high frequencies is commonly considered as a charge transfer resistance (R_{ct}) [66–68]. The charge transfer resistance must be corresponding to the resistance between metal and OHP (outer Helmholtz plane). And therefore, in the present investigation, the polarization resistance (R_p) which includes charge transfer resistance (R_{ct}) , diffuse layer resistance (R_d) , accumulation resistance (R_a) , film resistance (R_f) etc. is taken into the account [66–70]. The equivalent circuit shown in Fig. 5b was used to fit the experimental impedance data. The circuit comprises of a constant phase elements (*CPE*), a charge transfer resistance (R_p) and a solution resistance (R_s) . Generally, double layer formed by adsorption of inhibitors on the metallic surface behaves as CPE rather than pure capacitor and therefore, the capacitor was replaced by CPE to fit the semicircle impedance data more accurately [71]. The admittance (Y_{CPE}) and impedance (Z_{CPE}) of the CPE can be represented by following relation [72]:

$$Y_{\rm CPE} = Y_0 (j\omega)^n \tag{14}$$

and

$$Z_{\text{CPE}} = \left(\frac{1}{Y_0}\right) \left[(j\omega)_n \right]^{-1} \tag{15}$$

where, Y_0 is the *CPE* constant, ω is the angular frequency; *j* is the imaginary number (i.e. $j^2 = -1$) and *n* is the phase shift (exponent) which is related to the degree of surface inhomogeneity. The nature of *CPE* can be expressed by the values of *n*, *CPE* can represent resistance ($n = 0, Y_0 = R$), capacitance ($n = 1, Y_0 = C$), inductance ($n = -1, Y_0 = 1/L$) or Warburg impedance ($n = 0.5, Y_0 = W$). Where *W* is the Warburg impedance (*WZ*), which is related to the diffusion of the ions from the passive films of inhibitors. The values of *CPE* constant (Y_0), angular frequency (ω) and phase shift (n) were used to evaluate the values of C_{dl} with and without inhibitors as follows:

$$C_{\rm dl} = Y_0(\omega_{\rm max})^{n-1} \tag{16}$$

where, ω_{max} is the frequency at which the imaginary part of impedance has attained the maximum (rad s⁻¹) value. The derived impedance parameters are presented in Table 6. The inspection of the results shown in Table 6 it is obvious that values of *n* are almost constant and are equal/or more than 0.827 suggesting that the interface is of capacitive nature in the present study. The careful examination of the results shown in Table 6 shows that values of *R*p gradually increase with increasing inhibitors concentrations which is attributed due to adsorption inhibitors on metal surface which isolate the metal from electrolyte and protect from corrosion [66,73]. The decreased values of *C*_{d1} in presence of inhibitors are attributed due to decrease in dielectric constant and/or enhancement of the thickness of the electrical double layer or by combination of both [66,73].

Fig. 6 represents the Bode impedance and phase angle plots in absence and presence of different concentrations of the studied inhibitors. An ideal capacitor is characterized by a fixed value of slope (unity) and phase angle (-90°) in Bode plot [73,74]. The deviation from the ideal

Table 5

Tafel polarization parameters for mild steel in 1M HCl solution in absence and presence of different concentrations of AAIs.

Inhibitor	Conc (mM)	E _{corr} (mV/SCE)	$egin{smallmatrix} eta_{a} \ (\mu A/cm^2) \end{split}$	β_{c} (mV/dec)	i _{corr} (mV/dec)	η%	θ
Blank	_	- 445	70.5	114.6	1150	_	_
AAI-1	0.172	-498	70.5	151.3	473.4	58.83	0.5883
	0.345	-472	72.6	99.2	201.7	82.46	0.8246
	0.517	-549	83.8	126.8	136.2	88.15	0.8815
	0.689	-508	66.7	125.3	85.6	92.55	0.9255
AAI-2	0.172	-489	79.8	107.5	332.8	71.06	0.7106
	0.345	-498	73.3	143.9	178.6	84.46	0.8446
	0.517	-479	71.6	100.9	96.0	91.65	0.9165
	0.689	-495	71.1	157.2	58.9	94.87	0.9487
AAI-3	0.172	-498	79.6	107.4	296.7	74.20	0.7420
	0.345	-496	74.1	88.1	146.2	87.28	0.8728
	0.517	-514	90.6	128.4	74.4	93.53	0.9353
	0.689	-410	75.2	108.3	25.5	97.78	0.9778

capacitive behavior can be attributed to the surface inhomogeneity of structural and interfacial origin. Generally, the value of phase angle increases with increasing the metal surface smoothness. Careful visualization of the Bode plots shows that value of phase angle for free corroding specimen is much smaller ($\approx 40^{0}$) as compare to the values of phase angles for inhibited specimens. The increased values of phase angle in presence of different concentrations of the suggest that surface

roughness of mild steel surface decreased due to formation of protective film by inhibitors [73,74].

3.3. Surface measurements

3.3.1. Scanning electron microscopy (SEM)

The adsorption of the AAIs on metallic surface was also supported by SEM analysis. The SEM images of mild steel specimens in absence and presence of optimum concentrations of the studied inhibitors after 3 h immersion time are given in Fig. 7. Fig. 7a represents the SEM image of abraded mild steel specimen which is characterized by visual appearances of cracks and lines might be caused during abrasion by SiC emery papers. Further, it can be seen that SEM micrograph of mild steel in absence of inhibitors (Fig. 7b) is more corroded and damaged showing Mountain like appearance due to free acid corrosion in absence of inhibitors. However, in presence of optimum concentrations of inhibitors, the SEM micrographs show very remarkable change in the surface morphologies. The increased surface smoothness in presence of inhibitors is attributed due to adsorption of inhibitors on the metallic surfaces.

3.3.2. Atomic force microscopy (AFM) study

Fig. 8 shows the three dimensional views of the mild steel surfaces in the absence and presence of optimum concentration of each of the three studied inhibitors. Fig. 8a, which is highly corroded, rough, and inhomogeneous depicts the surface of mild steel retrieved from the uninhibited



Fig. 5. (a-c): Nyquist plots recorded for mild steel in 1M HCl in the absence and presence of different concentrations of (a) AAI-1, (b) AAI-2, and (c) AAI-3 (d) Equivalent circuit used for fitting and analyzing the electrochemical data.

acid solution. The calculated average surface roughness of the uninhibited mild steel specimen was 392 nm. However, in the presence of optimum concentration of studied inhibitors, surface morphology of mild steel specimens from the inhibitors containing aggressive media (Fig. 8b–d) remarkably improved owing to the formation of protective film on the surface. The calculated average surface roughnesses were 176, 143, and 118 nm in the presence of optimum concentration of AAI-1, AAI-2and AAI-3, respectively. The increased surface smoothness further suggested the formation of protective film of the inhibitors molecules on the steel surface, which prevents the metal from aggressive (direct) acid attack.

3.4. Theoretical studies

3.4.1. Quantum chemical calculations

The optimized molecular structures and the corresponding HOMO and LUMO electron density surfaces of the studied compounds are shown in Figs. 9 and 10. The electron distribution of HOMO gives information about the centers or the sites that are most likely to donate the electrons to the corresponding orbital of the acceptor molecule, whereas the electron distribution of the LUMO provides information about the centers of the molecule that are more likely to accept the electron from an appropriate donor molecule. Fig. 10 shows that the electron density of the HOMO mainly localized only over the indole rings in the AAI-1 and AAI-2, while for AAI-3 the electron density localized over the indole as well as phenyl rings. From the frontier molecular electron distribution it can be seen that as compare to AAI-1 and AAI-2, the involvement of the phenyl ring of AAI-3 helps in a greater electron transfer and therefore could adsorb more effectively on steel. The diethylamine and pyrrolidine residues of AAI-1 and AAI-2, respectively makes small contributions to the LUMO, as the electron density mainly localized over indole and phenyl rings. While the effectiveness of AAI-3 is due to the fact that piperdine ring make huge contribution to LUMO distribution.

The calculated values of some common quantum chemical calculations parameters are listed in Table 7. On the basis of earlier reports available in the literature it can be concluded that the value of $E_{\rm HOMO}$ of a molecule is a measure of the tendency to donate its HOMO electrons to the corresponding acceptor molecule [75,76]. The value of $E_{\rm HOMO}$ of the studied compounds follows the order: AAI-3 > AAI-2 > AAI-1, which is in accordance with the order of inhibition efficiency obtained experimentally. On the other hand, the $E_{\rm LUMO}$ is a parameter that defines the affinity of molecule to accept electrons into its LUMO from appropriate donor molecule [75,76]. The energy gap $\Delta E (E_{\rm LUMO}-E_{\rm HOMO})$ is another very important parameter which can be used to predict the reactivity of molecules. Generally a molecule with low value of ΔE associated with high chemical reactivity and therefore high inhibition

Table 6

EIS parameters obtained for mild steel in 1M HCl in absence and presence of different concentrations of AAIs.

Inhibitor	Conc (mM)	$R_{\rm s}$ (Ω	$R_{\rm p}$ (Ω	n	Y ₀ (μF	C _{dl} (µF	η %	θ
	. ,	cm ²)	cm ²)		cm ⁻²)	cm ⁻²)		
Blank	-	1.12	10.7	0.827	482.2	106.21	_	_
AAI-1	0.172	0.796	24.73	0.846	140.3	53.58	56.73	0.5673
	0.345	0.765	70.02	0.832	128.5	50.65	84.71	0.8471
	0.517	1.059	107.0	0.848	108.3	44.19	90.00	0.9000
	0.689	1.181	175.4	0.832	91.8	42.22	93.89	0.9389
AAI-2	0.172	0.987	31.97	0.842	138.7	51.71	66.53	0.6653
	0.345	0.743	75.89	0.843	115.8	48.41	85.90	0.8590
	0.517	0.892	121.3	0.866	96.21	43.52	91.17	0.9117
	0.689	0.811	234.3	0.845	84.3	41.07	95.43	0.9543
AAI-3	0.172	0.810	41.72	0.839	131.8	48.25	74.35	0.7435
	0.345	0.741	90.44	0.832	110.3	43.48	88.16	0.8816
	0.517	0.696	155.5	0.829	87.8	32.16	93.11	0.9311
	0.689	1.362	256.6	0.836	63.7	29.82	95.83	0.9583



Fig. 6. Bode impedance modulus $(\log f vs \log |Z|)$ and phase angle $(\log f vs \alpha^0)$ plots for mild steel in 1M HCl in the absence and different of different concentrations of (a) AAI-1, (b) AAI-2, and (c) AAI-3.



Fig. 7. SEM images of mild steel surfaces: abraded (a), in 1M HCl in the absence of AAIs (b), and in 1M HCl in the presence of optimum concentration of AAI-1 (c), AAI-2 and (d), AAI-3(e).

efficiency [77,78]. The trends of the ΔE obtained in the present study for investigated inhibitors are in good agreement with the order of experimental inhibition efficiencies. The global electronegativity (χ) is another important reactivity parameter that can be utilized to explain

the electron holding capacity of the molecule. Generally, higher value of χ is consistent with low electron transfer by the molecule and therefore low inhibition efficiency. In our present study, the values of χ obey the order (Table 7): AAI-1 > AAI-2 > AAI-3, which indicates that AAI-1



Fig. 8. AFM images of mild steel surfaces in 1M HCl in the absence of AAIs (a), and in 1M HCl in the containing optimum concentration of AAI-1 (b), AAI-2 and (c), AAI-3(d).

has lowest and AAI-3 has highest tendency of electrons donation to the appropriate acceptor (Fe) molecule. Further, inspection of the tabulated data show that the values of χ decreases with increasing the softness (σ) and decreasing the hardness (η) of the inhibitors molecules. And

therefore it can be concluded that electrons donation from inhibitors to metal increases with increasing the softness and decreases with increasing the hardness of the inhibitors. The values of the fraction of electron transferred (ΔN) form inhibitors to the metal were calculated and



Fig. 9. Optimized molecular structures of studied AAIs, (a) AAI-1, (b) AAI-2 and (c) AAI-3.



Fig. 10. The frontier molecular orbital (left-hand side: HOMO; and right-hand side: LUMO) of the studied APQDs (a) AAI-1 (b) AAI-2 and (c) AAI-3.

listed in Table 7 for all studied inhibitors. In the present case the ΔN values obey the order: AAI-3 > AAI-2 > AAI-1, which suggests that the maximum fraction of electron transfer occur in case of AAI-3 which

the lowest fraction of electrons transfer occur in case of AAI-1 among the studied inhibitors suggesting that AAI-3 would absorb most effectively on steel surface. The entire quantum chemical calculations results

Table 7
Quantum chemical parameters derived from the B3LYP/6-31 + $G(d,p)$ method.

Parameters → Inhibitors↓	μ (Debye)	E _{HOMO} (eV)	E _{LUMO} (eV)	Δ <i>E</i> (eV)	η (eV)	σ (eV)	χ (eV)	ΔN	ΔE_{T}
AAI-1	1.6927	- 8.5748	-5.1214	3.4534	1.7267	0.57913	6.8481	0.04398	-0.43167
AAI-2	1.9680	- 8.5628	-5.1124	3.4504	1.7252	0.57964	6.8376	0.04706	-0.43130
AAI-3	2.3671	- 7.8036	-5.1236	2.6800	1.3350	0.74903	6.4636	0.20014	-0.33375



Fig. 11. Side view equilibrium adsorption of AAI-1, AAI-2, and AAI-3 on Fe (110) surface (left hand side: before; and right hand side: after molecular dynamics simulations).

show that corrosion inhibition in the present study occur via electron transfer from high electron density of the inhibitors to the surface Fe atoms.

3.4.2. Molecular dynamics simulations

Recently, MD simulation has emerged as an indispensable tool in the characterization of the adsorption behavior of the inhibitor molecules

Table 8

Interaction energies between the inhibitors and Fe (110) surface (Kcal/mol).

Inhibitor	Ebinding	$E_{\text{interaction}} \left(-E_{\text{binding}} \right)$
AAI-1	137.53	- 137.53
AAI-2	142.79	- 142.79
AAI-3	144.82	- 144.82

on the metallic surface [79]. MD simulations can reasonably provide information of the most favorable configuration of adsorbed inhibitor molecule on the metal surface and have become a well-established tool in computational chemistry. In our present paper, MD simulations were carried out to study the adsorption characteristics of investigated inhibitors on the Fe (110) surface. The equilibrium configurations for all inhibitors are represented in Fig. 11. Careful inspection of the Fig. 11 shows that during the MD simulation process, the AAIs moved gradually near the Fe (110) surface with almost flat orientation. And, therefore it has been concluded that investigated inhibitors can be adsorbed on the mild steel surface through the phenyl and indole rings moieties. Furthermore, it has been reported that empty dorbitals of the surface Fe atoms can facilitate the adsorption process by accepting the electrons from the inhibitors molecules. In the studied compounds, the nonbonding electrons of the N atoms and π - electrons of the indole and phenyl moieties provide sufficient electronic density to transfer in the empty d-orbitals of the surface Fe atoms in order to form a stable coordinate bond. Generally, the adsorption energy is the energy released (or needed) when the relaxed adsorbate component is adsorbed on the substrate. The values of interaction energy $(E_{\text{interaction}})$ and binding energy (E_{binding}) between studied inhibitors and Fe (110) surface were evaluated when systems reach equilibrium. It can be seen from Table 8 that values of $E_{\text{Fe-AAIs}}(E_{\text{interaction}})$ are negative for all studied inhibitors which suggest that adsorption of these compounds on Fe (110) surface can take place spontaneously [80,81]. Moreover, it can also be observed from the results that AAI-3 has maximum negative value of E_{interaction} suggesting that it can be adsorbed on Fe surface most strongly and most efficiently and possess better inhibition efficiency among the studied inhibitors [80,81]. The value of the binding energies (E_{binding}) for different studied inhibitors follows the order: AAI-3 > AAI-2 > AAI-1, which is in accordance with order of their inhibition efficiencies obtained experimentally.

4. Conclusion

Three new 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3vl)(phenyl)methyl)-N-ethylethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) have been synthesized and investigated for their inhibition performances on mild steel corrosion in 1M HCl solution. The results of both gravimetric and electrochemical experiments showed that all the three compounds inhibit mild steel corrosion in 1M HCl solution and the inhibition efficiency increases with increasing concentration of the inhibitors. The effect of temperature on the inhibition activities of the studied compounds was investigated using gravimetric measurements and the results revealed that the inhibition efficiency of the compounds decreases with increase in temperature. The adsorption of studied AAIs obeys the Langmuir isotherm and involves competitive physisorption and chemisorption modes. Potentiodynamic polarization studies showed that the compounds inhibit both anodic and cathodic half reactions associated with corrosion process but their inhibition effects are more pronounced on the cathodic hydrogen gas evolution reaction. The EIS measurements showed that the compounds adsorb on mild steel surface to form protective film with essentially capacitive behavior. Surface morphology studies using SEM and AFM also provided some evidence of formation of protective film of AAIs on the steel surface. Quantum chemical parameters suggested the inhibition of mild steel corrosion in 1M HCl solution by the studied compounds is essentially due to effective transfer of electrons from the AAIs to Fe atom, which facilitates donor-acceptor interactions between the AAIs and the metal. Molecular dynamics simulations studies showed that the AAIs adsorbed the Fe (110) surface in a near flat orientation and the trends of the predicted interaction and binding energies of the equilibrium configurations are in good agreement with the order of experimental inhibition efficiency of the compounds. Both experimental and theoretical studies confirmed that the inhibition performances of the AAIs with cyclic amino substituents (AAI-2 and AAI-3) are higher than that of AAI-1 with an openedchain amino group. The inhibition potential was also found to increase with increasing ring size of the cyclic amine and this was attributed to increasing molecular size/volume of the molecule, which corresponds to increase in surface coverage.

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