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2-Amino-3-methyl-3-(4-nitrophenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile as effective corrosion inhibitor for mild steel in 1M HCl: Thermodynamical, electrochemical, surface and theoretical calculation

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Abstract Present work describes the corrosion inhibition efficiency of 2-amino-3-methyl-3-(4-nitro phenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile (INH) on mild steel in 1M HCl using weight loss, electrochemical, surface and molecular dynamics simulation methods. The weight loss results show that inhibition efficiency increasing with increasing INH concentration and maximum value was obtained at 50 mg/L concentration. Adsorption of the INH on mild steel surface obeys the Langmuir adsorption isotherm. Potentiodynamic polarization study suggests that investigated INH acts as mixed type inhibitor. EIS study indicates that the INH forms a protective surface film at metal/electrolyte interface. Both SEM and AFM studies show that surface smoothness increases due to formation of protective surface film by INH. The Monte Carlo simulation study suggests that INH has strong tendency to adsorb on mild steel surface in 1M HCl. The weight loss, electrochemical, surface and molecular dynamics calculations are in good agreement.

1. Introduction

Mild steel is one of the most important iron containing alloys used in different applications due to its excellent structural and mechanical strength [1]. However, due to its thermodynamical instability especially in aggressive acid solution it is very prone to corrosion [2]. The hydrochloric and sulfuric acids are two most commonly used acids in the industrial pickling of iron and its alloys to remove unwanted scales and rusts [3]. The poor corrosion resistance of mild steel in acidic solution needs

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utilization of corrosion inhibitors during such processes. Organic compounds containing heteroatoms (N, O, S, and P), heterocyclic rings, polar functional groups and extensive conjugation attract much attention as they inhibit metal corrosion by adsorbing on its surface via several adsorption centers [4]. Moreover, the adsorption on organic inhibitor on metal surface in acid solution depends upon several factors such as electronic structure of inhibitor molecule, steric factors, presence of functional groups (such as —OH, NH_2, —NO_2, —CO, —CN, —C═N—, —N═N—), nature of substituents present in the inhibitors, aromaticity, presence of conjugation, molecular weight, solution temperature and electrochemical potential at metal/electrolyte interfaces [5]. The literature survey reveals that inhibitors containing S (sulfur) and N (nitrogen) are useful in sulfuric and hydrochloric acid, respectively, whereas, inhibitor containing both N and S generally gives superior inhibition performance as compared to inhibitor containing only N or S [6]. Present study was undertaken to investigate the corrosion inhibition property of 2-amino-3-methyl-3-(4-nitrophenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile (INH) on mild steel surface in 1M HCl. The investigated inhibitor shows high inhibition efficiency due to presence of several polar functional groups (—NH_2, —CN, —NO_2) which increases the solubility as well as inhibition efficiency. Moreover, the —NH_2 group can easily protonate and form quaternary type of salt and enhance solubility of INH in acid solution. The study was performed using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and molecular dynamics simulation techniques. In the present study, we intended to find out some suitable molecular dynamic (MD) parameters such as total energy, adsorption energy, rigid adsorption energy, and deformation energy to describe the experimental inhibition efficiency of studied INH.

2. Experimental

2.1. Inhibitor synthesis

The INH used in the present study was synthesized by one step multi component coupling reaction of p-nitro acetophenone (1 mmol), malononitrile (2 mmol) and thiophenol (2 mmol) in the presence of triethyl amine as catalyst and water as solvent as described earlier [7] (Fig. 1). The characterization data of the synthesized compounds are as follows: INH 2-amino-3-methyl-3-(4-nitrophenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile: MP: 173–173 °C, IR (KBr, cm^{-1}): 3478, 3428, 3358, 3256, 3100, 2858, 2218, 1680, 1662, 1598, 1542, 1187, 1024, 710; ^{1}H NMR (300 MHz, DMSO, δ, ppm, Me_4Si): 1.63, 6.98, 7.32, 7.56, 7.89–8.13.

2.2. Preparation of electrodes and test solution

The mild steel specimens have chemical composition: (wt%): C = 0.076, Mn = 0.192, P = 0.012, Si = 0.026, Cr = 0.050, Al = 0.023, and remainder Fe was employed for all weight loss and electrochemical measurements. The mild steel specimens having dimension 2.5 × 2 × 0.025 cm were used for all weight loss experiments, whereas, mild steel having size 8 × 1 × 0.025 cm with exposed area 1 cm^2 was used for all electrochemical measurements. Before performing the experiments, the mild steel surface was successively cleaned with SiC emery papers of different grades (600, 800, 1000 and 1200), washed with double distilled water, degreased with acetone and finally dried under hot air blower. The test solution (1M HCl) was prepared by dilution of analytical grade HCl (MERCK, 37%) in double distilled water. The stock solution of inhibitor was prepared in 1M HCl containing 2% of acetone.

2.3. Weight loss experiments

The weight loss experiments were performed on rectangular mild steel specimens in the absence and presence of different concentration of the INH. The volume of solution was 100 ml and immersion time was 3 h. After completion of the immersion time the specimens were taken out, washed with double distilled water, degreased with acetone, ultrasonically cleaned with ethanol, dried and finally weighted accurately. All weight loss experiments were triply performed and mean value was reported to insure the reproducibility. Percentage inhibition efficiency (η%) was calculated using the following equation [8]:

$$\eta\% = \frac{w_0 - w_i}{w_0} \times 100 \quad (1)$$

where w_0 and w_i are the values of weight loss of mild steel in the absence and presence of INH, respectively. The corrosion rate (C_R) for mild steel corrosion was calculated using the following equation:

$$C_R\left(\text{mg cm}^{-2}\ h^{-1}\right) = \frac{87.6w}{AtD} \quad (2)$$

where w is the weight loss of mild steel (mg), A the area of the working electrode (cm^2), T is the exposure time (h) and D the density of working electrode (7.85 g cm^{-3}).

2.4. Electrochemical experiments

The Potentiostat/Galvanostat (Model G-300), with EIS software Gamry Instruments Inc., USA, containing three electrode electrolytic cell which consists of a pure platinum foil

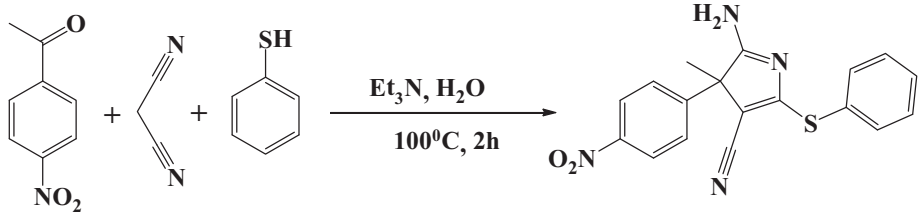

Figure 1 Synthetic scheme for investigated INH.

with exposed area 1 cm^2 as counter electrode, saturated calomel as reference electrode and mild steel with exposed area 1 cm^2 as working electrode was employed to carry out all electrochemical experiments. The all electrochemical data were analyzed by Echem Analyst 5.0 software package installed in the computer. Before performing the electrochemical measurements, the mild steel specimens were immersed in 1M HCl for 30 min to stabilize steady state potential. The potentials of working electrode were measured vs. a potential of saturated calomel electrode (SCE).

The potentiodynamic polarization studied was performed by automatically changing the working electrode potentials from −0.25 to +0.25 V vs corrosion potential (E_{corr}) at a scan rate of 1.0 mV s^{-1}. The linear segments of Tafel slopes were extrapolated to obtain corrosion current densities (i_{corr}), from which inhibition efficiency was calculated using the following formula [8]:

$$\eta\% = \frac{i^0_{corr} - i^i_{corr}}{i^0_{corr}} \times 100 \quad (3)$$

where i^0_{corr} and i^i_{corr} are the corrosion current densities in the absence and presence of INH, respectively.

The electrochemical impedance spectroscopy (EIS) experiments were carried out in between highest frequency limit of 100 kHz and lowest frequency limit of 0.01 Hz at open circuit potential with amplitude of 10 mV using AC signal. Charge transfer resistances were calculated from diameter of the Nyquist curves. The $\eta\%$ was calculated using the following relation [8]:

$$\eta\% = \frac{R^i_{ct} - R^0_{ct}}{R^i_{ct}} \times 100 \quad (4)$$

where R^0_{ct} and R^i_{ct} are the charge transfer resistance in the absence and presence of INH, respectively.

2.5. SEM

SEM studied was performed on the mild steel specimens after 3 h exposure time in 1M HCl in the absence and presence of optimum concentration of INH using SEM model Ziess Evo 50 XVP instrument with an accelerating voltage of 50 Kv at 500× magnification.

2.6. Atomic force microscopy

The surface morphology of mild steel was investigated using atomic force microscopy after 3 h immersion time at 308 K. The measurements were performed using a NT-MDT multimode AFM, Russia, controlled by Solver scanning probe microscope controller. 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^{-1} with NOVA programme was used for image interpretation. The scanning area in the images was 5 μm × 5 μm.

2.7. Molecular dynamics simulation measurements

The Monte Carlo simulation was carried out using Adsorption Locator module in Materials Studio 7.0 commercial software licensed from Accelrys Inc., USA. The Monte Carlo (MC) search was adopted to compute the low configuration adsorption energy of the interactions of the 2-amino-3-methyl-3-(4-nitrophenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile on clean iron surface. For the whole simulation procedure, the Universal Force Field (UFF) was used to optimize the structures of all components of the system of interest. The simulation was carried out with Fe (1 1 0) crystal with a slab of 5 Å in depth with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. The Fe (1 1 0) plane was next enlarged to a (8 × 8) super cell to provide a large surface for the interaction of the inhibitors. After that, a vacuum slab with 30 Å thickness was built above the Fe (1 1 0) plane [9].

3. Result and discussions

3.1. Weight loss measurements

3.1.1. Effect of INH concentration

The variation of inhibition efficiency with INH concentration is shown in Fig. 2a and various weight loss parameters such as corrosion rate (C_R), surface coverage (θ) and corresponding inhibition efficiency ($\eta\%$) are given in Table 1. From the results depicted in Table 1 it is observed that the $\eta\%$ increases with increasing INH concentration. The maximum value of η

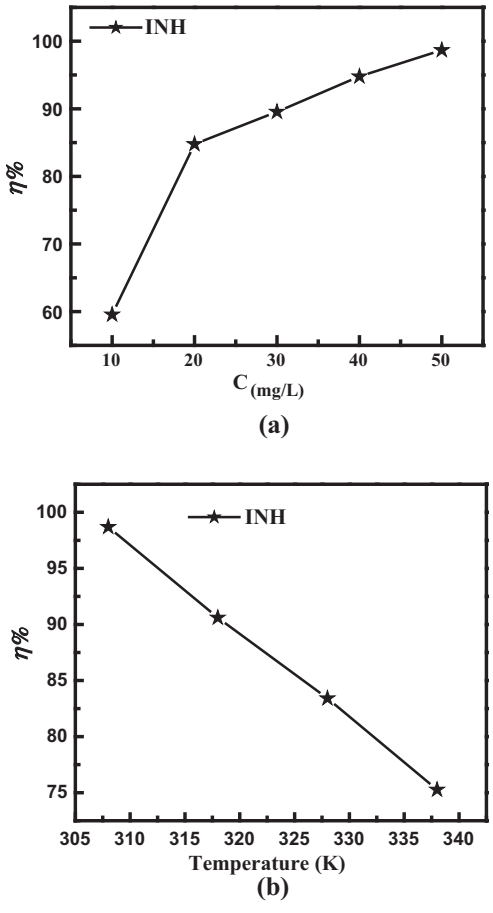

Figure 2 (a) Variation of inhibition efficiency with INH concentration. (b) Variation of inhibition efficiency with temperature.

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

Inhibitor	Conc (mg/L)	C_R (mg cm^{-2} h^{-1})	θ	η%
Blank	–	7.66	–	–
INH	10	3.10	0.5953	59.53
	20	1.16	0.8485	84.85
	30	0.80	0.8955	89.55
	40	0.40	0.9477	94.77
	50	0.10	0.9869	98.69

% was obtained at 50 mg/L concentration. Further increase in INH concentration does not cause any significant change in the inhibition performance suggesting that 50 mg/L is the optimum concentration. Increase in concentration, increases the effective surface coverage and therefore increases η%. On the basis of increase in inhibition efficiency with increasing INH concentration, it can be concluded that surface coverage and therefore inhibition efficiency increase with increasing inhibitor concentration. However, probably the maximum surface coverage was obtained at 50 mg/L concentration. Therefore, further increase in the concentration did not cause any significant increase in the surface coverage and inhibition efficiency by inhibitor.

3.1.2. Effect of temperature

Effect of solution temperature on corrosion inhibition efficiency of INH in 1M HCl is shown in Fig. 2b. It is observed that the value of η% decreases on increasing solution temperature. The increase in solution temperature increases the kinetic energy of the INH and therefore decreases the interaction between inhibitor and metal surface and thus decreases the inhibition efficiency [10]. Further, increases in the solution temperature cause molecular decomposition resulting into decrease in the inhibition efficiency. The effect of temperature on the nature of mild steel dissolution in 1M HCl can be best explained in terms of Arrhenius equation [11]:

$$\log(C_R) = \frac{-E_a}{2.303RT} + \log \lambda \quad (5)$$

where C_R is the corrosion rate in mg cm^{-2} h^{-1}, λ is the Arrhenius pre-exponential factor, R is the gas constant and T is the absolute temperature. The values of E_a with and without INH were calculated with the help of slopes and intercepts of the Arrhenius plots (Fig. 3) and are given in Table 2. From the results depicted in Table 2 it is observed that the value of E_a is higher (117.11 kJ/mol) in presence of INH as compared to value of E_a in the absence of INH (28.48 kJ/mol), suggesting that INH inhibits mild steel corrosion by forming an energy barrier for corrosion process [12]. Moreover, electrostatic interaction (physical adsorption) between charged inhibitor and charged metal surface might cause this increase in the value of E_a in the presence of INH [13].

3.1.3. Adsorption isotherm

The mechanism of corrosion inhibition in acid solution as well as basic interaction between metal and inhibitor can be explained in terms of molecular adsorption. The adsorption of inhibitor on metal surface creates a barrier between metal and electrolyte which isolate the metal from aggressive

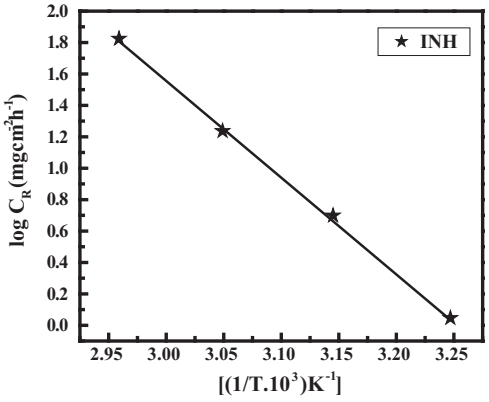

Figure 3 Arrhenius plots for the corrosion rate of mild steel versus the temperature in 1M HCl.

Table 2 Values of activation energies for mild steel dissolution in 1M HCl in the absence and presence of INH.

Inhibitor	ΔE
Blank	28.48
INH	117.11

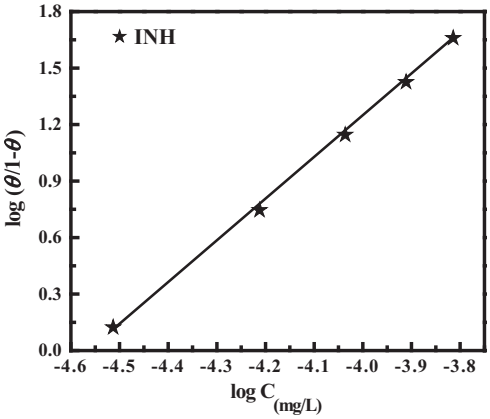

Figure 4 Langmuir isotherm plots for the adsorption of INH on mild steel surface in 1M HCl.

solution and protect from corrosion. In our present study several adsorption isotherms namely, Langmuir, Temkin, and Frumkin isotherms were tested to find best fit. The results showed that Langmuir isotherm gives the best fit with value of regression coefficient more close to unity (R^2 = 0.9999). The Langmuir isotherms can be best represented by the following relation [14]:

$$K_{ads}C = \frac{\theta}{1-\theta} \quad (6)$$

where C_{inh} is the concentration of inhibitor, θ is the degree of surface coverage at different concentrations of the INH and K_{ads} is the equilibrium constant for adsorption–desorption process. The Langmuir isotherm plot (Fig. 4) gives a straight line between log (θ/1 − θ) and log $C_{(mol/L)}$ for studied INH

Table 3 The values of K_{ads} and ΔG^0_{ads} for mild steel in 1M HCl at different studied temperature.

Inhibitor	K_{ads} (10^4 M^{-1})				$-\Delta G^0_{ads}$ (k J mol^{-1})			
	308	318	328	338	308	318	328	338
INH	9.043	1.157	0.603	0.365	39.52	35.36	34.70	34.34

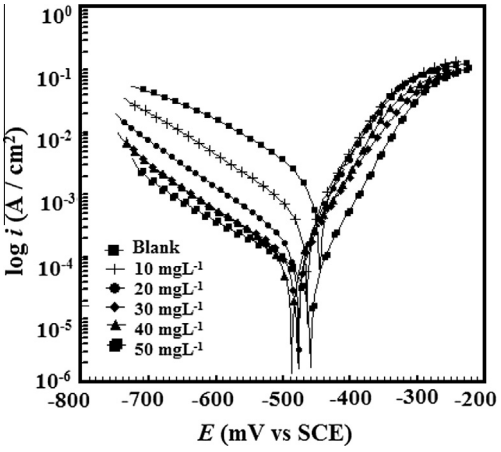

Figure 5 Polarization curves for mild in the absence and presence of different concentrations of INH.

with value of regression coefficient close to unity. The value of K_{ads} related to the free energy of adsorption $\Delta(G^0_{ads})$ is as bellows:

$$\Delta G^0_{ads} = -RT\ln(55.5K_{ads}) \quad (7)$$

where R is the universal gas constant, T is the absolute temperature in K, and the numerical value 55.5 represents the molar concentration of water in acid solution. The calculated values of K_{ads} and ΔG^0_{ads} are given in Table 3. Generally, the higher value of K_{ads} was associated with strong adsorption and therefore, higher η%. From Table 3 it is observed that values of ΔG^0_{ads} range between 39.52 kJ/mol and 34.34 kJ/mol. The negative values of ΔG^0_{ads} suggest that process of INH adsorption at mild steel surface in 1M HCl is spontaneous and mostly involves both physical and chemical interactions [15].

3.2. Electrochemical measurements

3.2.1. Potentiodynamic polarization measurements

The potentiodynamic nature of mild steel in 1M HCl in the absence and presence of various concentrations of INH is shown in Fig. 5. Several polarization parameters such as

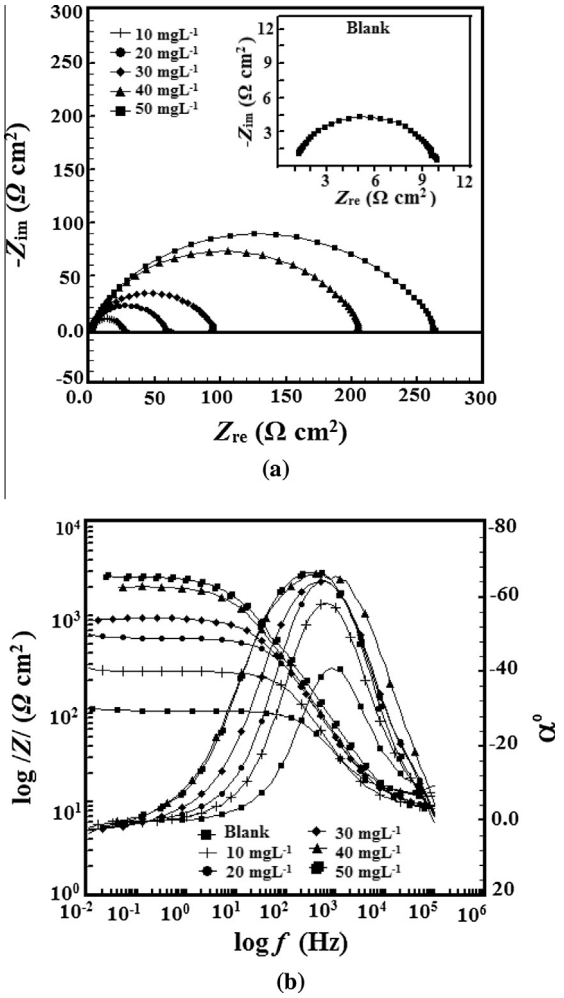

Figure 6 (a) Nyquist plot for mild steel in 1M HCl without and with different concentrations of INH. (b) Bode ($\log f$ vs $\log|Z|$) and phase angle ($\log f$ vs α^0) plots for mild steel in 1M HCl in the absence and presence of different concentration of INH.

corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes (β_a and β_c), surface coverage

Table 4 Tafel polarization parameters for mild steel in 1M HCl solution in the absence and at different concentrations of INH.

Inhibitor	Conc (mg/L)	E_{corr} (mV/SCE)	i_{corr} (μA/cm^2)	β_a (mV/dec)	β_c (mV/dec)	θ	η%
Blank	–	−445	1150	70.5	114.6	–	–
INH	10	−465	462.3	61.2	130.3	0.5980	59.80
	20	−477	174.2	56.8	134.4	0.8485	84.85
	30	−479	119.3	63.6	189.0	0.8962	89.62
	40	−487	63.2	63.3	132.7	0.9449	94.49
	50	−459	42.6	60.3	185.7	0.9629	96.29

Table 5 EIS parameters obtained for mild steel in 1M HCl without and with different concentration of INH.

Inhibitor	Conc (mg/L)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	n	θ	η%
Blank	–	1.12	9.58	106.21	0.827	–	–
INH	10	0.894	24.6	84.21	0.825	0.6105	61.05
	20	0.932	56.9	67.78	0.830	0.8316	83.16
	30	0.901	91.8	64.09	0.852	0.8956	89.56
	40	1.110	197.5	60.30	0.861	0.9514	95.14
	50	0.760	259.8	55.22	0.899	0.9631	96.31

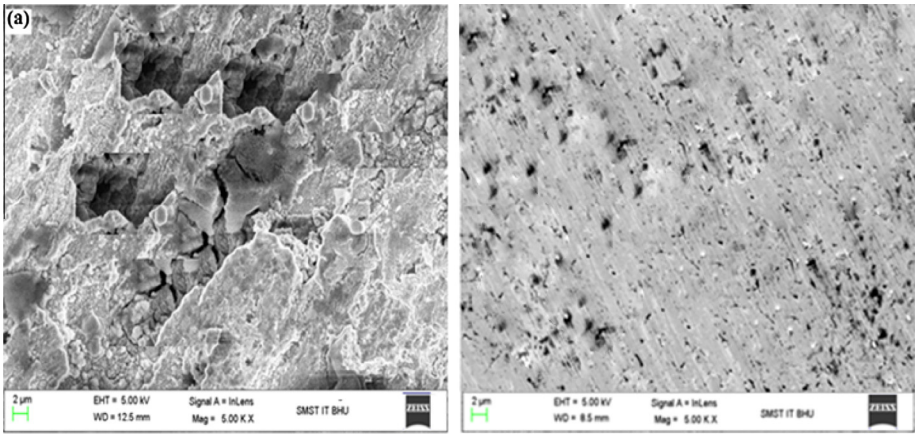

Figure 7 SEM images of mild steel (a) in blank acid solution and in the presence of 50 mg/L of (b) INH.

(θ) and corresponding inhibition efficiency (η%) were calculated by extrapolation of linear segments of anodic and cathodic Tafel slopes and are given in Table 4. From the results shown in Table, it is observed that the presence of INH in acid solution affects the anodic rate of mild steel dissolution as well as rate of cathodic hydrogen evolution without causing any substantial decrease in the value of E_{corr} suggesting that INH is a mixed type inhibitor [16,17]. Further, results showed that the presence of INH decreases the values of corrosion current density (i_{corr}) suggesting that rate of mild steel dissolution decreased in the presence of INH at various concentrations [18]. Further, decrease in i_{corr} values is more pronounced at higher INH concentration.

3.2.2. Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy is the most important electrochemical technique to study the kinetics and some structural properties of electric double layer. Fig. 6a shows the Nyquist plots for mild steel dissolution in the absence and presence of different concentrations of the INH. It is observed that diameter of the Nyquist plots increases with increasing INH concentration. Further, the Nyquist plots represent the imperfect semicircle which is attributed due to rough electrode surface and surface inhomogeneity. Several EIS parameters such as solution resistance (R_s), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), phase shift (n), surface coverage (θ) and corresponding inhibition efficiency (η%) were calculated using an equivalent circuit described elsewhere [19] and are given in Table 5. From the EIS depicted in Table 5 it is observed that values of R_{ct} increase whereas the values of C_{dl} decrease in the presence of INH at different concentration. This increase in R_{ct} and decrease in C_{dl} values in the presence of INH are attributed due to a decrease in local dielectric constant and/or to an increase in the thickness of the electrical double layer [20]. These results suggest that the studied INH inhibits mild steel corrosion by adsorbing at the metal/electrolyte interfaces.

The Bode plot (Fig. 6b) in the absence and presence of each studied concentration gives one time constant (single maximum) at intermediate frequencies. Broadening of the maximum is attributed due to adsorption of the INH at metal/electrolyte interface [19]. In the present investigation a linear relationship between log /Z/ and log$f$ with slope value close to -1 and phase angle value close to $-70°$ was observed in the Bode plots. An ideal capacitor is characterized by a constant value of phase angle and slope equal to $-90°$ and -1, respectively. The deviation from the ideal capacitive behavior in present study is attributed due to roughness of the mild steel surface [20]. The careful observation of the Bode plots shows that values of phase angle are higher for inhibited solution as compared to uninhibited solution. Moreover, it can be further observed that the values of phase angle for inhibited solution increase on increasing INH concentration. The increased values of phase angle in the presence of INH suggest that mild steel surface smoothness increased due to formation of protective surface film by INH [20,21].

3.3. Surface measurements

3.3.1. Scanning electron microscopy (SEM) study

The scanning electron microscopy (SEM) images of mild steel surface in the absence and presence of optimum concentration

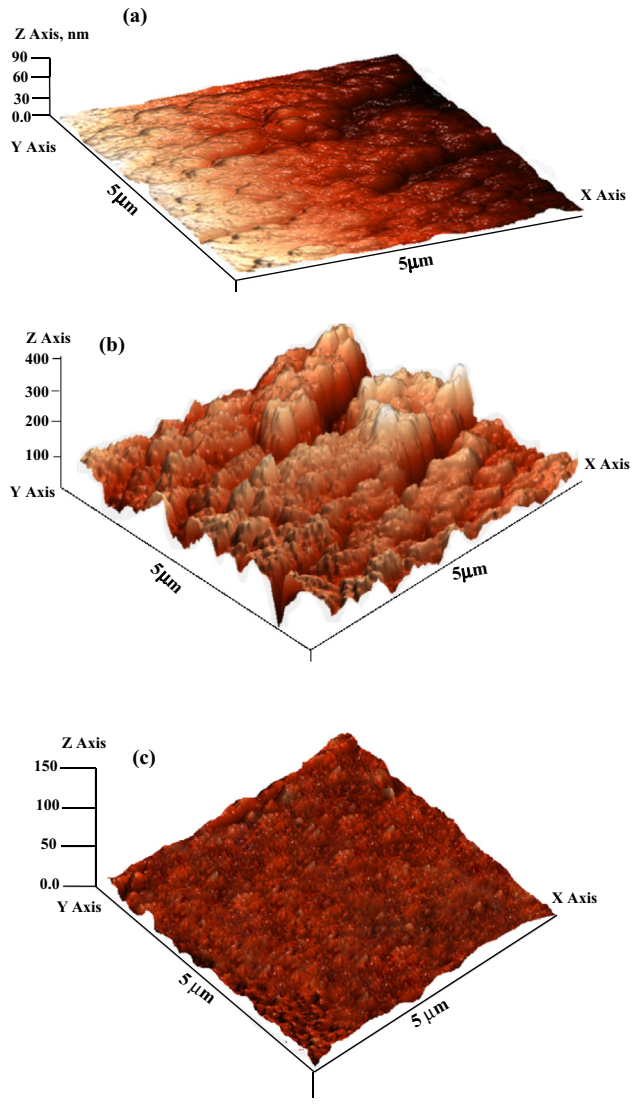

Figure 8 The AFM micrographs of mild steel surface (a) abraded mild steel, (b) in blank acid solution and (c) in presence of INH.

of the investigated INH are shown in Fig. 7. The SEM image of mild steel in the absence of INH (Fig. 7a) was highly corroded and damaged which might be attributed to the free acid corrosion of the surface in the absence of INH. However, in the presence of INH at its optimum concentration (Fig. 7b) the surface morphology remarkable smoothed owing to the formation of protective surface film by INH.

3.3.2. Atomic force microscopy (AFM) study

The atomic force microscopy (AFM) micrographs for abraded, uninhibited and inhibited mild steel specimens are shown in Fig. 8. Fig 8a represents the AFM micrographs of abraded mild steel surface characterized by clear appearance of bradding scratches on the surface resulted due to mechanical rubbing with SiC emery paper during cleaning process. The calculated surface roughness of abraded mild steel specimens was 85 nm. The AFM micrograph for uninhibited solution (Fig. 8b) was highly corroded with characteristic pits and cracks. The calculated surface roughness for uninhibited mild steel specimen was 392 nm. The higher surface roughness is attributed due to free acid corrosion of mild steel in the absence of INH. However, in the presence of INH at its optimum concentration the surface smoothness increases due to formation of protective surface film. In the presence of INH the average surface roughness of mild steel was 146 nm. The decrease in the surface roughness in the presence of INH (146 nm) than in absence of INH (392 nm) suggests that in the presence of INH surface of mild steel is less corroded and damaged due to formation of protective film by INH. However, the surface roughness is comparatively high in the presence of INH as compared to abraded mild steel surface which is attributed to some extent of corrosion even in the presence of INH.

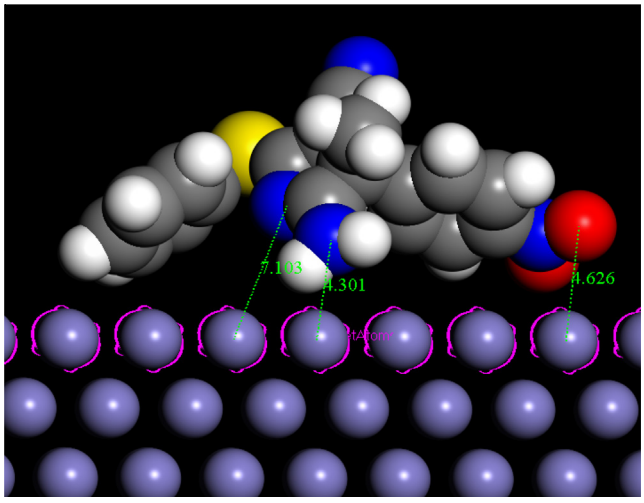

Figure 9 The most stable low energy configuration for the adsorption of INH on Fe (1 1 0) surface obtained through the Monte Carlo simulations.

3.4. Monte Carlo simulation

Recently, molecular dynamics simulation has been broadly used to describe the interaction between metal and inhibitor because it provides some essential parameters such as total energy, adsorption energy, and rigid adsorption energy. In our present study, the Monte Carlo simulation calculation was used to find the lowest energy for the investigated system. The outputs and descriptors calculated by the Monte Carlo

Table 6 Outputs and descriptors calculated by the Monte Carlo simulation for the lowest adsorption configurations of INH on Fe (1 1 0) surface (in kcal/mol).

Systems	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy	$dE_{ad}/dN_{i\ Inhibitors}$
Fe (1 1 0)/INH	56.486	−4.051	−4.196	0.014	−4.051

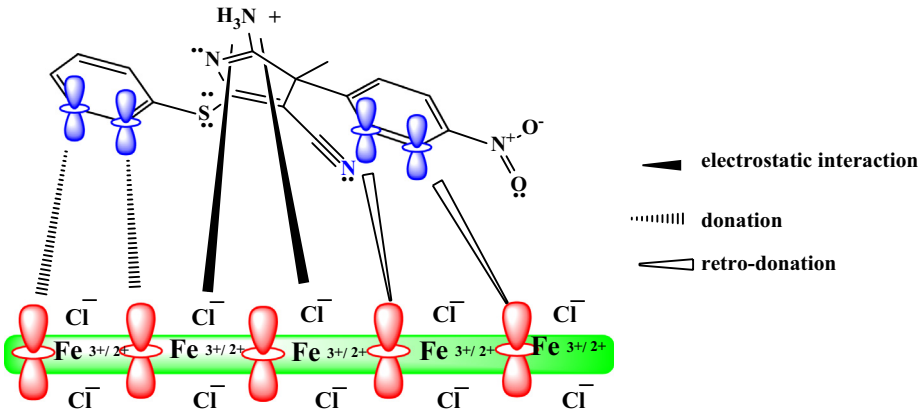

Figure 10 Pictorial representation of the adsorption behavior of the INH on mild steel in 1M HCl solution.

simulation, such as the total adsorption, adsorption energy, rigid adsorption and deformation energies are presented in Table 6. Fig. 9 represents the most stable low energy configuration for the adsorption of INH on Fe (1 1 0) surface obtained through the Monte Carlo simulations. The sum of rigid adsorption energy and deformation energy is defined as adsorption energy for the adsorbate component (INH), whereas, the rigid adsorption energy is the energy in kcal/mol which is either released or absorbed when the unrelaxed INH molecule was adsorbed on the Fe_2O_3 surface. The deformation energy is the energy (in kcal/mol) released when the adsorbed adsorbate components are relaxed on the Fe_2O_3 surface [22]. The quantity (dE_{ads}/dN_i) depicted in Table 6 represents the energy of Fe_2O_3-adsorbate configurations where one of the adsorbate components has been removed. The results depicted in Table 6 show that the INH was associated with high negative values of adsorption energy resulting in the strong interaction between metal and INH molecule [21].

4. Mechanism of inhibition

The mechanism of mild steel corrosion in the presence of 2-amino-3-methyl-3-(4-nitrophenyl)-5-(phenylthio)-3H-pyrrole-4-carbonitrile can be explained on the basis of molecular adsorption. The adsorption of organic inhibitor on metal surface may be either pure physical or pure chemical or the combination of both i.e. physiochemisorption [23]. Generally, physical adsorption involves electrostatic interaction between charged metal and charged inhibitor molecule whereas chemisorption involves sharing of charges between metal and inhibitor. It has been established that in acid solution heteroatoms (N, O, S, etc.) undergo easy protonation to give positively charged inhibitor. This positively charged inhibitor electrostatically interacts with negative charged mild steel surface (due to presence of surface chloride ions). However, after evolution of H_2 gas at cathode the cationic form of inhibitor returns to its neutral form. The neutral form of inhibitor adsorbs chemically by transfer of unshared paired electrons of heteroatoms in the d-orbital of the surface Fe- atoms (donation). However, this type of donation causes accumulation of excessive charges on the metal surface and to relief from excessive charges the transfer of electrons from d-orbital of the surface Fe-atoms in the π- antibonding molecular orbitals of the inhibitor takes place (retro-donation). This type donation and retro-donation strengthen each other through synergism [24,25]. The higher inhibition efficiency of the investigated INH can be explained on the basis of strong interaction between metal and INH through several polar groups (such as $-NO_2$, $-NH_2$, $-CN$), heteroatoms (N, O, S), and aromatic as well as hetero-aromatic rings. Further, the presence of polar functional groups and heteroatoms also increases the solubility of the INH in 1M HCl and therefore increases the inhibition efficiency [26]. A pictorial representation of the adsorption behavior of the INH on mild steel in 1M HCl solution is shown in Fig. 10.

5. Conclusion

From the above study it is concluded that 2-amino-3-methyl-3-(4-nitrophenyl)-5 (phenylthio)-3H-pyrrole-4-carbonitrile (INH) exhibited good inhibition efficiency on mild steel in 1M HCl. The inhibition efficiency increases on increasing INH concentration and maximum value was obtained at 50 mg/L concentration. The adsorption of INH on mild steel surface obeys the Langmuir adsorption isotherm. Potentiodynamic polarization study shows that studied INH is a mixed type inhibitor. EIS study shows that the INH forms a protective surface film on metal/electrolyte interface. The formation of protective surface film was further supported by SEM and AFM analysis. The molecular dynamics simulations study supports the weight loss, electrochemical and surface measurements and established that there is strong interaction between mild steel and the INH.

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