EL SEVIER



Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Application of new isonicotinamides as a corrosion inhibitor on mild steel in acidic medium: Electrochemical, SEM, EDX, AFM and DFT investigations



M. Yadav^{a,*}, R.R. Sinha^a, T.K. Sarkar^a, I. Bahadur^{b,*}, E.E. Ebenso^b

^a Department of Applied Chemistry, Indian School of Mines, Dhanbad 826004, India

^b Department of Chemistry, Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

ARTICLE INFO

Article history: Received 11 August 2015 Accepted 27 September 2015 Available online xxxx

Keywords: Mild steel Corrosion inhibition Isonicotinamides EIS SEM AFM DFT

ABSTRACT

Corrosion inhibition effect of 2-(2-(2-phenyl)-3-(isonicotinamido)-4-oxothiazolidin-5-yl) acetic acid (PITA) and N-(2-phenyl-4-oxothiazolidin-3-yl)-isonicotinamide (POTI) on mild steel corrosion in 15% HCl solution was studied by using weight loss, electrochemical polarization and electrochemical impedance spectroscopy (EIS) techniques. It was found that the inhibition efficiency of both inhibitors increases with increase in concentration. The effect of temperature on the corrosion rate was investigated and some thermodynamic parameters were calculated. Polarization studies show that both studied inhibitors are of mixed type in nature. The results show that both POTI and PITA are good inhibitors, and the adsorption of each inhibitor on mild steel surface obeys Langmuir adsorption isotherm. Scanning electron microscopic (SEM), energy dispersive X-ray spectroscopic (EDX) and atomic force microscopy (AFM) studies were used to characterize the surface morphology of uninhibited and inhibited mild steel specimens. The morphological study indicated adsorption of inhibitor molecules on the surface of the mild steel. The density functional theory (DFT) was employed for theoretical calculations. The results obtained from experimental measurements and those from theoretical calculations are in good agreement.

1. Introduction

Heterocyclic organic compounds containing sulfur, phosphorus, oxygen, nitrogen and aromatic rings are the most effective and efficient inhibitors for the metals in acidic medium [1–9]. Some of the heterocyclic compounds are of medicinal importance and have been successfully tested with various diseases and gained much importance as well. Nitrogen heterocycles have received attention towards pharmaceutical chemistry due to their diverse medicinal potential [10]. Amide bonds play a critical role in the field of chemistry and biology in determining structure and dynamics in small molecules as well as in large molecules such as 2-(2-(2phenyl)-3-(isonicotinamido)-4-oxothiazolidin-5-yl) acetic acid (PITA) and N-(2-phenyl-4-oxothiazolidin-3-yl)-isonicotinamide (POTI) which are considered to be heterocyclic compounds. An important aspect of the amide linkage is the partial double bond character that results from donation of lone-pair electron density from amide nitrogen to the carbonyl carbon. Due to this a significant high barrier C—N bond rotation is found to be in amine based compounds. Hence, the modified barrier possesses a number of structural and electronic properties which led to significant importance of theoretical and experimental interest [11–14].

* Corresponding authors.

Acid solutions are extensively used in a variety of industrial processes such as oil well acidification, acid pickling and acid cleaning [15], which generally lead to serious metallic corrosion. To minimize the effect of corrosion during these processes corrosion inhibitor is added to the acid solution. Use of corrosion inhibitor is one of the most economical and practical methods for minimizing and controlling corrosion process [16, 17]. The application of organic compounds containing nitrogen, oxygen and sulfur as corrosion inhibitor in acid medium is reported in literature [18–21]. Due to their industrial applications of corrosion inhibitors, researchers are looking for efficient and environment friendly inhibitors. Most of the corrosion inhibitors inhibit corrosion due to adsorption of inhibitor molecules on the metal surface. The nature of the inhibitor, surface state of the metal and excess charge of the metal surface will affect the adsorption behavior of inhibitor molecule on the metal surface [22].

Keeping in view the importance of corrosion inhibitors in various industries, the present work focused on synthesis of 2-(2-(2-phenyl)-3-(isonicotinamido)-4-oxothiazolidin-5-yl) acetic acid (PITA) and N-(2phenyl-4-oxothiazolidin-3-yl)-isonicotinamide (POTI) in the laboratory and evaluation of corrosion inhibition performance of these inhibitors on mild steel in 15% HCl solution by weight loss measurement, potentiodynamic polarization, electrochemical impedance measurement as well using quantum chemical calculations. To the best of our knowledge there is no any information available in open literature on studied compounds as a corrosion inhibitor for mild steel in acidic medium. The

E-mail addresses: yadavdrmahendra@yahoo.co.in, bahadur.indra@gmail.com (I. Bahadur).

present work is a continuation of our systematic studies on corrosion inhibition of mild steel in acidic environment by synthesized organic compounds [23–25].

2. Experimental

2.1. Mild steel samples

Mild steel specimen which contained C = 0.14 wt.%, Mn = 0.98 wt.%, Si = 0.033 wt.%, S = 0.018 wt.%, P = 0.026 wt.%, Cr-0.02 wt.% and remainder iron was used for corrosion studies. Mild steel coupons having dimension 6.0 cm \times 2.5 cm \times 0.1 cm and 1.0 cm \times 1.0 cm \times 0.1 cm were mechanically cut, abraded using emery papers of different grit sizes up to 1200 grit, polished with Al₂O₃ (1 μ m and then 0.3 μ m particle size) for weight loss measurement and electrochemical measurement studies respectively. The specimens were cleaned with distillate water and degreased with acetone, dried and stored in desiccator.

2.2. Test solution

The test solutions (15% HCl) were prepared by dilution of analytical grade 37% HCl (Ramkem) with double distilled water. The concentrations of the studied inhibitors ranged from 100 ppm to 400 ppm (mg L⁻¹) and the volume of test solution used for weight loss measurement and electrochemical studies was 500 mL and 150 mL, respectively.

2.3. Synthesis of corrosion inhibitors

The compounds 2-(2-(2-phenyl)-3-(isonicotinamido)-4-oxothiazolidin-5-yl) acetic acid (PITA) and N-(2-phenyl-4-oxothiazolidin-3-yl)isonicotinamide (POTI) were synthesized by the reported procedure [26] as shown in Scheme 1. To an equimolar methanolic solution of isonicotinic acid hydrazide (0.1 mol) and substituted benzaldehyde (0.1 mol), a few drops of glacial acetic acid were added. The mixture was then refluxed on water bath for 5–6 h. It was then allowed to cool, poured onto crushed ice and recrystallised from methanol. The resulting compound was *N'*-benzylidene isonicotinohydrazides. The compounds POTI and PITA were synthesized by heating mixture of *N'*benzylidene isonicotinohydrazides (0.01 mol) and thioglycolic acid (0.01 mol) or thiomalic acid (0.01 mol) on an oil-bath at 120–125°C for 12 h. The reaction mixture was cooled and treated with 10% sodium bicarbonate solution. The product was isolated and recrystallized from methanol–dioxane (4:1). The structures of the compounds were supported by their IR, ¹H-NMR and elemental analysis data and their purity was confirmed by thin layer chromatography (TLC). The IR and ¹HNMR spectra of PITA and POTI are shown in Fig. 1 and Fig. 2, respectively.

The analytical and spectral data of the synthesized compounds are given below:

• PITA.

Yield: 76%; elemental analysis: C, 57.14; H, 4.20; N, 11.76; S, 8.96. Found: C, 56.95; H, 4.16; N, 11.68; S, 8.92.

IR (cm – 1): 3310 (NH), 1710 (C=O, thiazolidinone), 1570, 1470 (C=CAr), 1680 (C=O). ¹ H-NMR (300 MHz, CDCl₃) δ : 9.1 (2 H, pyridine), 7.9 (2 H, pyridine), 8.1 (1 H, NH), 11.0 (1 H, COOH), 7.3 (5 H, phenyl), 3.8 (1 H, thiazolidine), 5.8 (1 H, thiazolidine), 2.9 (1 H, CH₂), 2.7 (1 H, CH₂).

• POTI.

Yield: 72%; elemental analysis: C, 60.20; H, 4.35; N, 14.05; S, 11.07. Found: C, 59.94; H, 4.32; N, 14.16; S, 10.58.

IR (cm − 1): 3320 (NH), 1720 (C=O, thiazolidinone), 1580, 1470 (C=CAr), 1690 (C=O).

¹ H-NMR (300 MHz, CDCl₃) δ : 9.2 (2 H, pyridine), 7.8 (2 H, pyridine), 8.0 (1 H, NH), 7.1 (5 H, phenyl), 3.3 (2 H, thiazolidine), 5.9 (1 H, thiazolidine).

2.4. Weight loss method

Gravimetric experiments were performed according to the standard methods [27]. The corrosion rate (*CR*), inhibition efficiency (η %) and surface coverage (θ) was determined by following equations:

$$CR(\mathrm{mmy}^{-1}) = \frac{8.76 \times 10^4 \times W}{D \times A \times t} \tag{1}$$



Scheme 1. Synthetic route and structure of 2-(2-(2-phenyl)-3-(isonicotinamido)-4-oxothiazolidin-5-yl) acetic acid (PITA) and N-(2-phenyl-4-oxothiazolidin-3-yl)-isonicotinamide (POTI).



Fig. 1. IR spectra of PITA and POTI.

where, W = weight loss (g), A = area of specimen (cm²) exposed in acidic solution, t = exposure time (h), and D = density of mild steel (g cm⁻³);

$$\theta = \frac{CR_0 - CR_i}{CR_0} \tag{2}$$

$$\eta(\%) = \frac{CR_0 - CR_i}{CR_0} \times 100 \tag{3}$$

where, CR_0 and CR_i are corrosion rate in the absence and presence of inhibitors. This experiment was repeated at different temperatures of 30, 40, 50 and 60 °C by using water circulated Ultra thermostat to determine the temperature dependence of the inhibition efficiency.



Fig. 2. ¹H NMR spectra of PITA and POTI.

2.5. Electrochemical method

The electrochemical studies were conducted in a conventional threeelectrode cell consisting of mild steel sample of 1 cm² exposed area as working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode, using CH electrochemical workstation (Model No: CHI 760D, manufactured by CH Instruments, Austin, USA) at 303 K. Potentiodynamic polarization curves were obtained in the potential range from -250 to +250 mV vs. SCE at OCP at a scan rate of 1 mVs⁻¹. The linear Tafel segments of anodic and cathodic curves were extrapolated to obtain corrosion current densities (i_{corr}). The percentage inhibition efficiency (η %), was calculated using the equation:

$$\eta(\%) = \frac{i_{\rm corr}^0 - i_{\rm corr}}{i_{\rm corr}^0} \times 100 \tag{4}$$

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

Electrochemical impedance measurements were carried out using AC signals of amplitude 10 mV peak to peak at the open circuit potential in the frequency range of 100 kHz to 10 mHz. All impedance data were fitted to appropriate equivalent circuits using ZSimpWin.3.21 software. The inhibition efficiency (η %) was calculated from charge transfer resistance values obtained from impedance measurements using the following relation:

$$\eta(\%) = \frac{R_{\text{ct (inh)}} - R_{\text{ct}}}{R_{\text{ct (inh)}}} \times 100$$
(5)

where $R_{ct(inh)}$ and R_{ct} are charge transfer resistance in the presence and absence of inhibitor respectively. The values of double layer capacitance (C_{dl}) were calculated from charge transfer resistance and CPE parameters (Y_0 and n) using the expression [28]:

$$C_{dl} = \left(Y_0 R_{ct}^{1-n}\right)^{1/n} \tag{6}$$

where Y_0 is CPE constant and n is CPE exponent. The value of n represents the deviation from the ideal behavior and it lies between 0 and 1.

Conc. (ppm)	303 K			313 K			323 K			333 K		
	$CR (mmy^{-1})$	θ	η %	$CR (mmy^{-1})$	θ	η %	$CR (mmy^{-1})$	θ	η%	CR (mmy ⁻¹)	θ	η%
Blank	28.2	-	-	58.1	-	-	98.9	-	-	144.5	-	-
PITA												
100	5.80	0.794	79.41	13.35	0.770	77.02	26.59	0.731	73.11	45.83	0.682	68.28
200	3.22	0.885	88.58	7.83	0.865	86.51	16.88	0.829	82.93	31.67	0.780	78.08
300	1.29	0.954	95.41	3.12	0.946	94.62	8.87	0.910	91.03	18.91	0.869	86.91
400	1.07	0.962	96.18	2.82	0.951	95.13	7.04	0.928	92.87	15.83	0.890	89.04
POTI												
100	7.55	0.732	73.21	16.83	0.710	71.02	32.45	0.671	67.18	55.73	0.614	61.43
200	5.06	0.820	82.05	11.51	0.801	80.18	22.92	0.768	76.82	41.09	0.715	71.56
300	1.93	0.931	93.15	4.77	0.917	91.78	12.83	0.870	87.02	24.43	0.830	83.08
400	1.59	0.943	94.34	3.92	0.932	93.24	9.36	0.905	90.53	21.34	0.852	85.23

Corrosion parameters of mild steel in 15% HCI solution in the presence and absence of inhibitor at different temperatures, obtained from weight loss measurements.

2.6. Scanning electron microscopic and energy dispersive spectroscopy analysis

Table 1

For surface morphological study of the uninhibited and inhibited mild steel samples, SEM and EDX images were recorded using the instrument HITACHI S3400N.



Fig. 3. Arrhenius plots of log *CR* versus 1000/*T* for mild steel corrosion in 15% HCl solution (a) PITA (b) POTI.

2.7. Atomic force microscopy

The AFM images of polished, uninhibited and inhibited mild steel samples were carried out using a Nanosurf Easyscan2 instrument, Model: NT-MDT, Russia; Solver Pro-47.

2.8. Quantum chemical study

Complete geometrical optimizations of the investigated molecules are performed using density functional theory (DFT) with the Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) with 6-31G (d, p) basis set is implemented in Gaussian 03 program package [29,30]. Theoretical parameters such as the energies of the highest occupied and lowest unoccupied molecular orbital ($E_{\rm HOMO}$ and $E_{\rm LUMO}$), energy gap (ΔE) and dipole moment (μ) were determined.

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration and temperature

Corrosion parameters namely, corrosion rate (*CR*), surface coverage (θ) and inhibition efficiency (η %) of mild steel in 15% HCl solution in the absence and presence of different concentrations (100–400 ppm) of inhibitor at different temperatures (303 K–333 K), obtained from weight loss measurements are shown in Table 1. From Table 1, it is apparent that inhibition efficiency increased with increasing the concentration of the inhibitors. The inhibition efficiency of PITA and POTI at 400 ppm was found to be 96.18% and 94.34% respectively, at 303 K (Table 1). The increase in inhibition efficiency with increasing concentration of inhibitors is due to increase in the surface coverage, resulting retardation of metal dissolution [25].

Table 2

Activation parameter for mild steel in 15% HCl solution in the absence and presence of inhibitor obtained from weight loss measurements.

Inhibitor	Concentration (ppm)	E_a (kJmol ⁻¹)	$\Delta H^*(kJ/mol)$	$\Delta S^*(\text{Jmol}^{-1}\text{K}^{-1})$
Blank	-	45.78	43.13	-74.45
PITA	100	57.98	55.34	-47.51
	200	64.14	61.50	-32.18
	300	72.95	71.53	-4.18
	400	73.80	73.80	-2.80
POTI	100	55.96	53.34	-52.05
	200	58.62	56.00	-46.69
	300	72.33	70.09	-10.12
	400	72.72	69.71	-9.55

It is also clear from the Table 1 that the inhibition efficiency decreased with increasing temperature from 303 K to 333 K. Such type of behavior can be described on the basis that the increase in temperature leads to a shift of the equilibrium constant towards desorption of the inhibitors molecules at the surface of mild steel [31]. The inhibition efficiency of PITA is greater than POTI at all concentrations and temperatures.

3.1.2. Thermodynamic and activation parameters

To evaluate the adsorption and thermodynamic activation parameters of corrosion processes of mild steel in15% HCl solution, weight loss measurements were carried out in the temperature range 303– 333 K in the absence and presence of inhibitors after 6 h of immersion time. The values of the apparent activation energy (E_a) were calculated using the Arrhenius equation:

$$\log CR = \frac{-E_{a}}{2.303RT} + \log A \tag{7}$$

where E_a is the apparent activation energy, R is the molar gas constant (8.314 J K⁻¹mol⁻¹), T is the absolute temperature (K) and A is the Arrhenius pre-exponential factor. Fig. 3 (a, b) presents the Arrhenius plot of log *CR* against 1/*T* for the corrosion of mild steel in 15% HCl solution in the absence and presence of inhibitors PITA and POTI at concentrations ranging from 100 to 300 ppm. From Fig. 3 (a, b), the activation



Fig. 4. Transition state plot of log *CR/T* versus 1000/*T* for mild steel in 15% HCl solution at different concentrations of (a) PITA (b) POTI.

energy was calculated using the expression $E_a = -(\text{slope}) \times 2.303\text{R}$. The calculated values of E_a are summarized in Table 2. It is evident from Table 2 that the values of the apparent activation energy for the inhibited solutions were higher than that for the uninhibited solution, indicating that the dissolution of mild steel was decreased due to formation of a barrier by the adsorption of the inhibitors on metal surface [32].

The values of standard enthalpy of activation (ΔH^*) and standard entropy of activation (ΔS^*) were calculated by using the transition state equation:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$
(8)

where, h is Planck's constant and N is the Avogadro number.

A plot of log (*CR*/*T*) against 1/*T* (Fig. 4 a, b) gave straight lines with a slope of $-\Delta H^*/2.303R$ and an intercept of $[\log(R/Nh) + \Delta S^*/(2.303R)]$, from which the activation thermodynamic parameters ΔH^* and ΔS^* were calculated, as listed in Table 2. The values of E_a and ΔH^* are close to each other, as expected from the concept of transition-state theory, and follow the same pattern of variation with different concentrations of the inhibitor. The negative value of ΔS^* for both inhibitors indicates that the formation of the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of the transition from reactants to activated complex [33].



Fig. 5. Langmuir plots of (C_{inh}/θ) versus C_{inh} for (a) PITA (b) POTI.

Table 3					
Adsorption para	ameters for PITA and POTI for	r mild steel in 15% HC	l solution at a temperature ra	ange of 303–333	К.
Inhibitor	Temperature (K)	$K (M^{-1})$	ΛC° . (kI mol ⁻¹)	Slone	p ²

Inhibitor	Temperature (K)	$K_{\rm ads}$ (M ⁻¹)	ΔG°_{ads} (kJ mol ⁻¹)	Slope	R^2	ΔH°_{ads} (kJ mol ⁻¹)	ΔS°_{ads} (J mol ⁻¹ K ⁻¹)
	303	$5.2 imes 10^5$	-37.5	0.998	0.994		
	313	$2.4 imes 10^5$	-36.8	0.996	0.996		
	323	$1.3 imes 10^5$	-36.2	0.994	0.995	-64.47	-89
PITA	333	$0.6 imes 10^5$	-35.4	0.992	0.991		
	303	$4.4 imes 10^5$	-37.1	0.997	0.992		
	313	$2.1 imes 10^5$	-36.3	0.994	0.993	-61.04	-79
	323	$1.03 imes 10^5$	-35.6	0.993	0.996		
POTI	333	$0.5 imes 10^5$	-34.7	0.991	0.997		

3.1.3. Adsorption isotherm

The interaction between the inhibitor and mild steel surface can be very well understood in terms of the adsorption isotherm. Attempts were made to fit experimental data to various isotherms including Frumkin, Langmuir, Temkin, and Freundlich. The results were best fitted by the Langmuir adsorption isotherm:

$$\frac{C_{\rm inh}}{\theta} = \frac{1}{K_{\rm ads}} + C_{\rm inh} \tag{9}$$

where, C_{inh} is the inhibitor concentration, K_{ads} is the equilibrium constant for adsorption–desorption process. Plotting C_{inh}/θ vs. C_{inh} yielded a straight line [Fig. 5] with a correlation coefficient (R^2) and slope values given in Table 3 at different temperatures. The R^2 and slope values in Table 3 are near to unity indicating that the adsorption of these inhibitors obeys the Langmuir adsorption isotherm.

The values of K_{ads} were calculated from the intercept of Fig. 5. Large values of K_{ads} were obtained for both studied inhibitors suggesting more efficient adsorption and hence better corrosion inhibition efficiency. Using the values of K_{ads} , the values of ΔG_{ads} were obtained by using the following equation:

$$\Delta G_{\rm ads}^0 = -RT \ln(55.5K_{\rm ads}) \tag{10}$$

where *R* is the gas constant and *T* is the absolute temperature (K). The value of 55.5 is the concentration of water in solution in mol L⁻¹. Calculated values of K_{ads} and ΔG°_{ads} are listed in Table 3. The negative values of ΔG°_{ads} reveal the spontaneity of adsorption process. In general, values of ΔG°_{ads} up to -20 kJmol⁻¹ are compatible with physisorption and those which are more negative than -40 kJmol⁻¹ involve chemisorptions [34]. The calculated ΔG°_{ads} values for PITA and POTI were found in the range of -35.4 to -37.5 and -34.7 to -37.1 kJmol⁻¹, respectively, at different temperatures (303–333 K), these values were between the threshold values for physical adsorption and chemical



Fig. 6. The relationship between ΔG^0_{ads} and temperature.

adsorption, indicating that the adsorption process of these inhibitors at mild steel surface involves both the physical as well as chemical adsorption. It is apparent from Table 3 that, the negative value of ΔG^0_{ads} decreased on increasing the temperatures, suggesting that the adsorption of inhibitor molecules on mild steel surface is not favorable with increasing experimental temperature, indicating that physisorption has the major contribution while chemisorption has the minor contribution in the adsorption process.

The nature of adsorption (physisorption or chemisorptions or both) of inhibitor on the surface of mild steel can be determined on the basis of the values of enthalpy of adsorption (ΔH^0_{ads}) for the inhibitors. The enthalpy and entropy changes for the adsorption of inhibitors (PITA



Fig. 7. Potentiodynamic polarization curves for mild steel in 15% HCl solution in the presence and absence of inhibitor at 303 K. (a) PITA (b) POTI.

Table 4
Electrochemical parameter for mild steel in 15% HCl solution in the presence or absence of inhibitor at 303 K

Conc.	Tafel extrapolation	on data							EIS data	ì	
(ppm)	E _{corr} (V vs SCE)	$\beta_{\rm a} ({\rm mV}{\rm dec}^{-1})$	$-\beta_{\rm c}$ (mV dec ⁻¹)	$i_{\rm corr}$ ($\mu { m Acm}^{-2}$)	η %	$R_s (\Omega \text{ cm}^2)$	$R_{\rm ct} (\Omega { m cm}^2)$	$Y_0 (\mu { m Fcm}^{-2})$	n	$C_{\rm dl}$ (µF cm ²)	η %
Blank	-495	103	182	10.0	-	1.02	2.7	483	0.852	168	-
PITA											
100	-431	111	176	1.94	80.6	0.89	15.1	159	0.876	67.8	82.00
200	-437	92	184	1.29	87.1	0.68	22.0	108	0.892	51.9	87.77
300	-439	103	169	0.52	94.8	0.93	45.4	43	0.927	26.3	94.00
POTI											
100	-435	87	181	2.70	74.1	0.95	11.0	219	0.868	87.5	75.45
200	-438	103	172	1.67	83.3	0.83	17.2	137	0.884	61.8	84.12
300	-442	94	158	1.24	93.2	0.77	35.0	60	0.927	32.8	92.22

and POTI) on mild steel surface were determined from the basic thermodynamic equation [35]:

$$\Delta G^{0}_{ads} = \Delta H^{0}_{ads} - T \Delta S^{0}_{ads} \tag{11}$$

where ΔH^0_{ads} and ΔS^0_{ads} are the standard enthalpy and entropy changes of adsorption process, respectively. The plot of ΔG^0_{ads} versus *T* was linear (Fig. 6) with the slope equal to $-\Delta S^0_{ads}$ and intercept of ΔH^0_{ads} . The calculated values of ΔH^0_{ads} and ΔS^0_{ads} are listed in Table 3. The ΔH_{ads} values are negative for both studied inhibitors, which suggests that the adsorption of inhibitor's molecules on mild steel surface is an exothermic process. It has been reported in literature that an



Fig. 8. Nyquist plot for mild steel in 15% HCl solution containing various concentrations of (a) PITA (b) POTI at 303 K.



Fig. 9. Equivalent circuit applied for fitting of the impedance spectra.



Fig. 10. Bode plots for mild steel in a 15% HCl solution in the absence and presence of different concentrations of inhibitors (a) PITA (b) POTI.

endothermic adsorption process ($\Delta H_{ads} > 0$) is due to chemisorption while an exothermic adsorption process ($\Delta H_{ads} < 0$) may be attributed to physisorption, chemisorption or a mixture of both [36]. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of ΔH_{ads} , it is lower than 40 kJ mol⁻¹ for the physisorption process whereas for chemisorption process approaches 100 kJ mol⁻¹. In the present study, H_{ads} values for PITA and POTI are -64.47 kJ mol⁻¹ and -61.04 kJ mol⁻¹ respectively, which are larger than the common physical adsorption heat, but smaller than the common chemical adsorption heat, emphasizing that mixed type (both physical and chemical) adsorption takes place. The similar results were also reported by other authors [37–39].

The negative value of ΔS^0_{ads} obtained for adsorption of both the inhibitors as shown in Table 3 suggests that before the adsorption of inhibitor's molecules on the mild steel surface, inhibitor molecules might freely move in the bulk solution, but with the progress in the adsorption, inhibitor molecules were orderly adsorbed on the mild steel surface, as a result a decrease in entropy is observed [40]. From the thermodynamic principles, since the adsorption is an exothermic process, it must be accompanied by a decrease of entropy [41].

3.2. Electrochemical measurements

3.2.1. Potentiodynamic polarization studies

Potentiodynamic polarization experiments were undertaken to distinguish the effect of both inhibitors on the anodic dissolution of mild steel and cathodic hydrogen ion reduction. Typical potentiodynamic polarization curves for mild steel in 15% HCl in the absence and presence of different concentration of inhibitors are shown in Fig. 7 (a, b), while the electrochemical parameters derived from the polarization curves are summarized in Table 4. Addition of the inhibitors (PITA and POTI) is seen to affect the anodic as well as the cathodic partial reactions, shifting the corrosion potential (E_{corr}) slightly towards more positive (anodic) values and reducing the anodic and cathodic current densities and the corresponding corrosion current density (i_{corr}). This indicates that both inhibitors functioned as mixed-type inhibitors in 15% HCl solution [42].

The reduction in the value of corrosion current density in the presence of inhibitor is more pronounced with the increasing inhibitor concentrations, which results in increase in inhibition efficiency. The inhibitor molecules are first adsorbed on the mild steel surface, blocking the available reaction sites, and decrease the corrosion current density.

3.2.2. Electrochemical impedance spectroscopy (EIS) studies

Electrochemical impedance measurements were undertaken to provide information on the kinetics of the electrochemical processes at the mild steel/acid interface and how this is modified by the presence of inhibitor. Nyquist plots for mild steel corrosion in 15% HCl solution in the absence and presence of different concentrations (100-300 ppm) of the inhibitors PITA and POTI are given in Fig. 8 (a, b), respectively. The Nyquist plots show single semicircles for all systems over the frequency range studied, corresponding to one time constant. The impedance spectra were analyzed by fitting to the equivalent circuit model shown in Fig. 9, which has been used previously to adequately model the mild steel/acid interface [43]. In this equivalent circuit, the solution resistance is shorted by a constant phase element (CPE) that is placed in parallel to the charge transfer resistance. The CPE is used in place of a capacitor to compensate deviations from ideal dielectric behavior arising from the inhomogeneous nature of the electrode surfaces [44]. The impedance of the CPE is given by

$$Z_{CPE} = Y_0 - -1(j\omega)^{-n}$$
(12)

where Y_0 and n stand for the CPE constant and exponent, respectively, $j = (-1)^{1/2}$ is an imaginary number, and ω is the angular frequency in rad s⁻¹ ($\omega = 2\pi f$), where *f* is the frequency in Hz. The corresponding electrochemical parameters are presented in Table 4 and reveal that the both inhibitors increased the magnitude of R_{ct} , with corresponding



Fig. 11. SEM image of mild steel in 15% HCl solution after 6 h immersion at 303 K (a) before immersion (polished), (b) after immersion without inhibitor (c) with 300 ppm PITA (d) with 300 ppm POTI.



Fig. 12. EDX spectra of mild steel specimens (a) polished, (b) after immersion without inhibitor (c) with 300 ppm PITA (d) with 300 ppm POTI.

decrease in the double layer capacitance ($C_{\rm dl}$). The increase in $R_{\rm ct}$ values in inhibited systems, which corresponds to an increase in the diameter of the Nyquist semicircle, confirms the corrosion inhibiting effect of both inhibitors. The observed decrease in $C_{\rm dl}$ values, which normally results from a decrease in the dielectric constant and/or an increase in the double-layer thickness, can be attributed to the adsorption of inhibitor molecules (with lower dielectric constant compared to the displaced adsorbed water molecules) onto the metal/electrolyte interface, thereby protecting the metal from corrosive attack [45].

The Bode phase angle plots (Fig. 10 a, b) show single maximum (one time constant) at intermediate frequencies, broadening of this maximum in the presence of inhibitors accounts for the formation of a protective layer on the electrode surface. Moreover, there is only one phase maximum in Bode plot (Fig. 10 a, b) for both inhibitors, which indicates only one relaxation process, which would be the charge transfer process, taking place at the metal–electrolyte interface.

Fig. 10 (a, b) shows that the impedance value in the presence of both inhibitors is larger than in absence of inhibitors and the value of impedance increases on increasing the concentration of both studied inhibitors. These mean that the corrosion rate is reduced in the presence of the inhibitors and continued to decreasing on increasing the concentration of inhibitors.

Electrochemical results (η %) are in good agreement with the results (η %) obtained by weight loss experiment.

3.3. Scanning electron microscopy

Morphological studies of the surfaces of mild steel specimens in uninhibited and inhibited acid were analyzed by SEM after immersion in the different test solutions for 6 h at 303 K. SEM images of polished sample, uninhibited sample and inhibited samples are shown in Fig. 11 (ad). The morphology of the polished mild steel specimen (Fig. 11 a) is very smooth and shows no corrosion while mild steel specimen dipped in 15% HCl solution in the absence of inhibitor (Fig. 11 b) is very rough and the surface is damaged due to metal dissolution. However, the presence of 300 ppm of inhibitor (PITA, POTI) suppresses the rate of corrosion and surface damage has been diminished considerably (Figs. 11 c, d) as compared to the blank solution (Fig. 11 b) suggesting formation of a protective inhibitor film at the mild steel surface.

3.4. Energy dispersive spectroscopy

Energy dispersive X-ray analysis (EDX) technique was employed in order to get information about the composition of the surface of the mild steel sample in the absence and presence of inhibitors in 15% HCI solution. The results of EDX spectra are shown in Fig. 12 (a–d). The percentage atomic content of various elements of the polished, uninhibited and inhibited mild steel surface determined by EDX is shown in Table 5. The percentage atomic content of Fe for mild steel immersed in 15% HCI

Table 5
Percentage atomic contents of elements obtained from EDX spectra.

Inhibitors	Fe	С	S	Cr	Mn	Cl	Ν	0
Polished mild steel	85.26	12.46	-	0.86	0.46	-	-	-
Mild steel in blank HCl	83.12	15.68	-	0.67	0.28	2.29	-	6.36
Mild steel in PITA	69.24	19.26	1.72	0.56	-	0.31	3.42	13.28
Mild steel in POTI	71.23	19.36	1.68	0.54	-	0.32	3.42	10.62



Fig. 13. Atomic force micrographs of mild steel surface (a) polished mild steel, (b) mild steel in 15% HCl solution and (c) in the presence of inhibitor POTI (d) PITA.



Fig. 14. The optimized structure (left) and HOMO (center) and LUMO (right) distribution for inhibitors in gaseous state (a) PITA (b) POTI [atom legend: white = H; gray = C; blue = N; red = 0].

Table 6

POTI

-4.442

Inhibitor	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm LUMO}~(\rm eV)$	$\Delta E (eV)$	$\mu(D)$
PITA	-4.443	- 1.684	2.759	2.32
POTI	-4.648	- 1.636	3.012	2.40

Table 7 Quantum chemical parameters for PITA and POTI in aqueous media.							
Inhibitor	$E_{\rm HOMO}~(\rm eV)$	E_{LUMO} (eV)	$\Delta E (eV)$	μ(D)			
PITA	-4.124	- 1.862	2.262	2.86			

solution is 83.12%, and those for mild steel dipped in an optimum concentration (300 ppm) of POTI and PITA are 71.23% and 69.24%, respectively. From Fig. 12 (a-d) it is apparent that the spectra of inhibited samples show suppressed Fe peaks, when compared with the polished and uninhibited mild steel sample. This suppression of Fe lines is due to the inhibitory film formed on the mild steel surface. The EDX spectra of inhibited mild steel contain the peaks corresponding to all the elements present in the inhibitor molecules indicating the adsorption of inhibitor molecules at the surface of mild steel.

- 1.746

2.696

2.62

3.5. Atomic force microscopy

The three-dimensional AFM images of polished, uninhibited and inhibited mild steel samples are shown in Fig. 13 (a-d). The average roughness of polished mild steel sample (Fig. 13 a) and mild steel sample in 15% HCl solution without inhibitor (Fig. 13 b) were found as 25 and 650 nm. It is clearly shown in Fig. 13 (b) that mild steel sample is badly damaged due to the acid attack on surface. However, in the presence of optimum concentration (300 ppm) of POTI and PITA as shown in Fig. 13 (c, d), the average roughness were reduced to 160 and 150 nm, respectively. The lower value of roughness for PITA than POTI reveals that PITA protects the mild steel surface more efficiently than POTI in 15% HCl solution.

3.6. Quantum chemical analysis

In order to study the effect of molecular structure on the inhibition efficiency, quantum chemical calculations were performed by using DFT and all the calculations were carried out with the help of complete geometry optimization. The optimized geometry, E_{HOMO} and E_{LUMO} of PITA and POTI in gaseous and aqueous media are shown in Figs. 14(a, b) and 15(a, b) respectively. As per the frontier molecular orbital theory, frontier molecular orbital's HOMO and LUMO are involved in the course of adsorption of the inhibitor molecules [46]. In general the higher the value of HOMO, the higher would be the electron donating capacity of the inhibitor to vacant d-orbital of the metal. And the lower the value of LUMO, the greater would be the electron accepting ability of the inhibitor from the filled metal orbitals. But the most important parameter is ΔE , which is the energy difference between LUMO and HOMO. The lower the value of ΔE the easier would be the release of electron and the stronger would the adsorption [47]. Thus to become a good corrosion inhibitor, easy donation of electron as well as easy acceptance of electron in their vacant orbital's is necessary [48]. The quantum chemical parameters for PITA and POTI in gaseous and aqueous media are represented in Tables 6 & 7 respectively. See Fig. 15

3.6.1. Gaseous PITA and POTI

In gaseous state inhibitor molecules act as neutral molecules. The inspection of Table 6 reveals that the *E*_{HOMO} values of PITA are greater than POTI, thus PITA has more electron donating capacity than POTI. Also E_{LUMO} value of PITA is lower than POTI, which makes PITA to accept more electron than POTI from filled d-orbital of mild steel and causes its stronger adsorption. The ΔE value of PITA is lower than POTI, which causes PITA to release electron easily and intern to strengthen its adsorption. So, overall the adsorption order can be given as follows: PITA > POTI. The adsorption process is occurring through transfer of lone pair of electrons of the inhibitor molecules to the vacant d-orbital of the metal causing chemisorptions nature of adsorption.



Fig. 15. The optimized structure (left) and HOMO (center) and LUMO (right) distribution for inhibitors in aqueous media for PITA and POTI [atom legend; white = H; Gray = C; blue = N; red = 0].



Fig. 16. The schematic illustration of different modes of adsorption on metal/acid interface.

3.6.2. Aqueous media PITA and POTI

In aqueous media there is the possibility of the inhibitor molecules to undergo protonation through negatively charged nitrogen atom. The protonated inhibitor molecules then adsorb over the mild steel surface. The quantum chemical parameters of the inhibitors in aqueous media are reported in Table 7. Observing Table 7, we could say that in aqueous media E_{HOMO} values for both the inhibitors (PITA and POTI) are higher than in gaseous state, this indicates that the protonation of inhibitors occurs and protonated inhibitors have greater tendency to donate electrons, and thus their adsorption capacity over mild steel surface is more. Also ΔE values in protonated inhibitors are less as compared to the neutral one, which suggests that protonated inhibitors have more reaction capacity than the neutral one. So, overall in the aqueous media protonated inhibitors have more interaction ability than neutral inhibitors. The values of magnetic moment (μ) for both inhibitors in aqueous media are higher than in gaseous state indicating the higher electrostatic force of attraction due to protonation of inhibitor molecules resulting physisorption nature of adsorption. This statement supports that both chemisorption and physisorption mechanisms have taken place over mild steel surface and this also supports the statement said in Section 3.1.3. So, pictorially the adsorption of both inhibitors on mild steel surface can be given (Fig. 16).

3.7. Mechanism of inhibition

Corrosion inhibition of mild steel in hydrochloric acid solution by different inhibitors (PITA and POTI) can be explained on the basis of molecular adsorption. These compounds inhibit corrosion by controlling both anodic as well as cathodic reactions. In acidic solutions these inhibitors exist as protonated species. In both inhibitors the nitrogen atoms present in the molecules can be easily protonated in acidic solution and convert into quaternary compounds. These protonated species adsorbed on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic site occurs through π -electrons of oxothiazolidine ring, phenyl ring and lone pair of electrons of nitrogen and oxygen atoms present in both the inhibitors PITA and POTI are expected to get adsorbed on the surface of mild steel through the lone pairs of electrons on N and O atoms and delocalized π -electron density on the oxothiazolidine and phenyl rings.

4. Conclusions

 PITA and POTI acted as efficient corrosion inhibitor for mild steel in 15% HCl solution.

- In the presence of both inhibitors, charge transfer resistance increases and double layer capacitance decreases due to adsorption of the inhibitor molecules on the surface of mild steel.
- The potentiodynamic polarization curves showed that both inhibitors act as mixed type inhibitors.
- The SEM, EDX and AFM investigations indicated that the inhibitor molecules are adsorbed on the mild steel surface and protected the mild steel against corrosion.

Acknowledgments

The authors acknowledge funding from North-West University and Department of Science and Technology and the National Research Foundation (DST/NRF) South Africa grant (Grant UID: 92333) for postdoctoral scholarship of Dr. I. Bahadur.

References

- [1] L.J. Berchmans, V. Sivan, S.V.K. Iyer, Mater. Chem. Phys. 98 (2006) 395–400.
- [2] X.H. Li, G.N. Mu, Appl. Surf. Sci. 252 (2005) 1254–1265.
- [3] R. Solmaz, G. Kardas, B. Yazicl, M. Erbil, Colloids Surf. A Physicochem. Eng. Asp. 312 (2008) 7–17.
- [4] M. Abdallah, Corros. Sci. 44 (2002) 717-728.
- [5] S.L. Granese, B.M. Rosales, C. Oviedo, J.O. Zerbino, Corros. Sci. 33 (1992) 1439–1453.
- [6] G. Subramaniam, K. Balasubramaniam, P. Shridhar, Corros. Sci. 30 (1990) 1019–1023.
- [7] E. Stupnisek-Lisac, M. Metikos-Hukovic, D. Lencic, J. Vorkapic-Furac, K. Berkovic, Corrosion 48 (1992) 924–930.
- [8] S.N. Raicheva, B.V. Áleksiev, E.I. Sokolova, Corros. Sci. 34 (1993) 343-350
- [9] S.M.A. Hossini, M. Salari, Indian J. Chem. Technol. 16 (2009) 480–485.
- [10] J.W. Dhore, G.B. Pethe, S.P. Wagh, G.D. Thorat, Arch. Appl. Sci. Res. 3 (2011) 407-414.
- [11] A. Taha, N.J. True, Phys. Chem. A 104 (2000) 2985–2993.
- [12] W.E. Stewart, T.H. Siddall, Chem. Rev. 70 (1970) 517-551
- [13] J.L. Avalos, J.D. Boeke, C. Wolberger, Mol. Cell 13 (2004) 639–648.
- [14] B.D. Smith, D.M. Goodenough-Lashua, C.J.E. D'Souza, K.J. Norton, L.M. Schmidt, J.C. Tung, Tetrahedron Lett. 45 (2004) 2747–2749.
- [15] H. Keles, M. Keles, L. Dehri, O. Serindağ, Mater. Chem. Phys. 112 (2008) 173–179.
- [16] V.S. Sastri, Corrosion Inhibitors Principles and Applications, John Wiley & Sons, New York, 1998.
- [17] S.S.A.A. El-Rehim, M.A.M. Ibrahim, K.F. Khaled, J. Appl. Electrochem. 29 (1999) 593–599.
- [18] L.M. Vracar, D.M. Drazic, Corros. Sci. 44 (2002) 1669-1680.
- [19] M. Behpour, S.M. Ghoreishi, N. Soltani, M. Salavati-Niasari, Corros. Sci. 51 (2009) 1073-1082.
- [20] Y.M. Tang, X.Y. Yang, W.Z. Yang, R. Wan, Y.Z. Chen, X.S. Yin, Corros. Sci. 52 (2010) 1801–1808.
- [21] H. Chang, W.Y. Shi, J.L. Shao, Q. Xu, Int. J. Electrochem. Sci. 7 (2012) 5626–5632.
 [22] J.Z. Ai, X.P. Guo, J.E. Qu, Z.Y. Chen, J.S. Zheng, Colloids Surf. A Physicochem. Eng. Asp.
- 281 (2006) 147–155.
 [23] M. Yadav, D. Sharma, S. Kumar, S. Kumar, I. Bahadur, E.E. Ebenso, Int. J. Electrochem. Sci. 9 (2014) 6580–6593.
- [24] M. Yadav, S. Kumar, N. Kumari, I. Bahadur, E.E. Ebenso, Int. J. Electrochem. Sci. 10 (2015) 602–624.

- [25] M. Yadav, S. Kumar, I. Bahadur, D. Ramjugernath, Int. J. Electrochem. Sci. 9 (2014) 6529-6550.
- [26] S.J. Gilani, S.A. Khan, O. Alam, V. Singh, A. Arora, J. Serb. Chem. Soc. 76 (2011) 1057-1067
- [27] ASTM, G 31–72, American Society for Testing and Materials, Philadelphia, PA, 1990.
 [28] M. Lebrini, F. Robert, A. Lecante, C. Roos, Corros. Sci. 53 (2011) 687–695.
- [29] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789.
 [30] A.D. Becke, J. Chem. Phys. 98 (1993) 1372–1377.
- [30] L. Fragoza-Mar, O. Olivares-Xometl, M.A. Domínguez-Aguilar, E.A. Flores, P. Arellanes-Lozada, F. Jimenez-Cruz, Corros. Sci. 61 (2012) 171–184.
- [32] I. Dehri, M. Ozcan, Mater. Chem. Phys. 98 (2006) 316-323.
- [33] X. Wang, H. Yang, F. Wang, Corros. Sci. 53 (2010) 510–523.
 [34] M. Behpour, S.M. Ghoreishi, N. Soltani, M. Salavati-Niasari, M. Hamadanian, A. Gandomi, Corros, Sci. 50 (2008) 2172–2181.
 [35] A.M. Badiea, K.N. Mohana, Corros. Sci. 51 (2009) 2231–2241.
- [36] F. Bentiss, M. Lebrini, M. Lagrenee, Corros. Sci. 47 (2005) 2915–2931.

- [37] L. Tang, G. Mu, G. Liu, *Corros. Sci.* 45 (2003) 2251–2262.
 [38] X. Li, G. Mu, Appl. Surf. Sci. 252 (2005) 1254–1265.
- [39] M. Benabdellah, R. Touzani, A. Dafali, M. Hammouti, S. El Kadiri, Mater. Lett. 61 (2007) 1197-1204.
- [40] G. Mu, X. Li, G. Liu, Corros. Sci. 47 (2005) 1932–1952.
- [41] J.M. Thomas, W.J. Thomas, Introduction to the Principles of Heterogeneous Catalysis, fifth ed. Academic Press, London, 1981 14.
- [42] C. Cao, Corros, Sci. 38 (1996) 2073–2082.
- [43] E.E. Oguzie, S.G. Wang, Y. Li, F.H. Wang, J. Phys, Chem. C 113 (2009) 8420–8429.
- [44] M. Lebrini, M. Lagrenée, H. Vezin, M. Traisnel, F. Bentiss, Corros. Sci. 49 (2007)
- 2254-2269.
- [45] A. Popova, E. Sokolova, S. Raicheva, M. Christov, Corros. Sci. 45 (2003) 33-58.
- [46] J. Fang, J. Li, J. Mol. Struct. 593 (2002) 179–185.
- [47] M.A. Amin, K.F. Khaled, Q. Mohsen, H.A. Arida, Corros. Sci. 52 (2010) 1684-1695.
- [48] J. Zhang, J. Liu, W. Yu, Y. Yan, L. You, L. Liu, Corros. Sci. 52 (2010) 2059–2065.