Electrochemical and Quantum Chemical Studies on Adsorption and Corrosion Inhibition Performance of Quinoline -Thiazole Derivatives on Mild Steel in Hydrochloric Acid Solution

Mahendra Yadav^{1,*}, Sushil Kumar¹, Debasis Behera¹, Indra Bahadur², Deresh Ramjugernath^{2,*}

¹Department of Applied Chemistry, Indian School of Mines, Dhanbad, 826004, India ²Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban, 4041, South Africa *E-mail: <u>yadav_drmahendra@yahoo.co.in; ramjuger@ukzn.ac.za;</u>

Received: 8 February 2014 / Accepted: 7 May 2014 / Published: 16 June 2014

In the present study two quinoline-thiazole derivatives namely, {4-[1-aza-2-(phenyl)vinyl]-3-phenyl-2thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl))vinyl] (Inh I) and {4-[1-aza-2-(4methoxyphenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2 chloro (3 quinolyl))vinyl] (Inh II) were synthesized and investigated as an inhibitor for mild steel corrosion in 15% HCl solution by using weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The inhibitors Inh I and Inh II show corrosion inhibition efficiencies of 81.5% and 84.0% at a 20 ppm concentration and 95.0% and 96.3% at a 200 ppm concentration, respectively, at 333 K. It was found that the inhibition efficiency of both the inhibitors increases with an increase in temperature and concentration of inhibitors. Polarization studies show that both the studied inhibitors are of mixed type in nature. The adsorption of inhibitors on the mild steel surface obeys the Langmuir adsorption isotherm. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed for the surface study of uninhibited and inhibited mild steel samples. The semi-empirical AM1 method was employed for theoretical calculations.

Keywords: Quinoline-thiazole derivatives, Mild steel, Corrosion inhibition, Hydrochloric acid, EIS,

Quantum chemical studies.

1. INTRODUCTION

Due to excellent mechanical properties and low cost, mild steel is used applied as a construction material in a large number of industries. Hydrochloric acid solutions are commonly used

for pickling, industrial acid cleaning, acid de-scaling, and oil well acidifying processes. Because of the aggressiveness of acid solutions, mild steel corrodes severely during these processes, which results in terrible waste of both resources and money. A corrosion inhibitor is often added to mitigate the corrosion of metal by acid attack. The selection of inhibitor is controlled by its economic availability, its efficiency to inhibit the substrate material and its environmental side effects. Most of the inhibitors for corrosion of steel in acidic media are organic compounds containing nitrogen, oxygen and/or sulfur atoms [1-8]. The inhibiting action of these compounds is due to the adsorption of these compounds onto the metal/solution interface. The adsorption process depends upon the nature and surface charge of the metal, the type of aggressive media, the structure of the inhibitor, and the nature of its interaction with the metal surface [9].

Some derivatives of quinolone [10-13] and thiazole [14-16] have been reported as good inhibitors for metals and alloys in hydrochloric acid solution, and exhibit different inhibition performance with the difference in substituent groups and substituent positions on the aromatic rings. The quinoline-thiazole derivatives contain quinoline and thiazole rings as two anchoring sites suitable for adsorption with the metal surface. Thus, it was expected that quinoline-thiazole derivatives would work as good corrosion inhibitors for mild steel in a hydrochloric acid solution.

In continuation of our research for developing corrosion inhibitors [4, 6-8] with high effectiveness and efficiency, the present paper explores a systematic study to ascertain the inhibitive action of synthesized quinoline-thiazole derivatives namely, {4-[1-aza-2-(phenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl))vinyl] (Inh I) and {4-[1-aza-2-(4-methoxyphenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl)) vinyl] (Inh II) on corrosion of mild steel in 15% HCl solution by using weight loss measurement, potentiodynamic polarization, AC impedance, and quantum chemical calculations. Two derivatives of quinoline-thiazole were used to discuss the effect of electron donating (-OCH₃) substituents present in the inhibitor molecule on inhibition efficiency of the inhibitor.

2. EXPERIMENTAL PROCEDURES

2.1. Synthesis of inhibitors

The compounds {4-[1-aza-2-(aryl) vinyl]-3-phenyl-2-thioxo (1, 3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro (3-quinolyl)) vinyl] were synthesized by the reported method [17] as shown in Scheme 1.



Scheme 1. Synthetic route of inhibitors (Inh I- {4-[1-aza-2-(phenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl))vinyl], Inh II- {4-[1-aza-2-(4-methoxyphenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl)) vinyl]).

The compound 2-chloroquinoline-3-carbaldehyde (1) reacts with 2-cyanoacetohydrazide in ethanol to form 1-[1-aza-2-(2-chloro (3-quinolyl)) vinyl]-2-cyanoacetamide (2). Phenyl isothiocyanate is added to a stirred solution of compound 2, in the presence of sulphur and triethylamine in a mixed solvent of dimethylformamide: ethanol (1:1) to form 1-[1-aza-2-(2-chloro(3-quinolyl))vinyl](4-amino-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)) carboxamide (3). Compound 3 reacts with different aldehydes in ethanol to yield {4-[1-aza-2-(aryl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3quinolyl))vinyl]carboxamides. The purity of the synthesized compounds was checked by thin layer chromatography (TLC). The structure of Inh I and Inh II is shown in Figure 1.



Inh I

Inh II

Figure 1. Structures of inhibitors (Inh I- {4-[1-aza-2-(phenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl))vinyl], Inh II- {4-[1-aza-2-(4-methoxyphenyl)vinyl]-3phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl)) vinyl]).

2.2. Mild steel sample

Corrosion studies were performed on mild steel samples having composition (wt. %): C, 0.12; Mn, 0.11; Cu, 0.01; Si, 0.02; Sn, 0.01; P, 0.02; Ni, 0.02 and the remainder Fe. Mild steel coupons having a dimension 6.0 cm \times 2.5 cm \times 0.1 cm were mechanically cut and abraded with different grades of emery paper (120, 220, 400, 600, 800, 1500 and 2000 grade) for weight loss experiments. For electrochemical measurements mild steel coupons having a dimension 1.0 cm \times 1.0 cm \times 0.1 cm were mechanically cut and abraded similarly to the previous procedure, with an exposed area of 1 cm² (rest covered with araldite resin) with a 3 cm long stem. Prior to the experiment, specimens were washed with distilled water, degreased in acetone, dried and stored in a vacuum desiccator.

2.3. Test solution

Analytical reagent (AR) grade HCl was diluted with triply distilled water to obtain 15% HCl solution. The concentration of inhibitors employed was varied from 20 to 200 ppm (mg L^{-1}), and the volume of electrolyte used was 250 mL.

2.4. Methods

2.4.1. Weight loss method

Weight loss measurements were performed at 303 K by immersing accurately weighed mild steel test coupons in 250 mL of 15% HCl solution in the absence and in the presence of 20, 50, 100, 150 and 200 ppm (mgL⁻¹) of the inhibitors. The immersion time was optimized and the optimized immersion time (6 h) was uniformly used for weight loss measurements. The test coupons were then removed from the electrolyte, washed thoroughly with distilled water, dried and weighed. Experiments in triplicate were conducted for each concentration of the inhibitor for the reproducibility, and the average of weight losses were taken to calculate the corrosion rate and inhibition efficiency of the

inhibitors. The corrosion rate (*CR*) and inhibition efficiency (η %) were determined by the following equations [18]:

$$CR\left(\mathrm{mmy}^{-1}\right) = \frac{87.6W}{Atd} \tag{1}$$

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

$$\eta(\%) = \frac{CR_0 - CR_i}{CR_0} \times 100$$
(2)

where, CR_0 and CR_i are the corrosion rates in the absence and presence of inhibitors. This experiment was repeated at different temperature of 303, 313, 323 and 333 K by using a water circulated Ultra thermostat to determine the temperature dependence of the inhibition efficiency.

2.4.2. Electrochemical method

Electrochemical polarization measurements were carried out in a conventional three-electrode cell consisting of a mild steel working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as reference electrodes, using CH electrochemical workstation (Model No: CHI 760D, manufactured by CH Instruments, Austin, USA) at 303 K. Before starting the experiments, the working electrodes were immersed in the test solution for 30 min until a steady state open circuit potential (E_{ocp}) reached. The mild steel surface was exposed (1 cm²) to various concentrations (20-200 ppm by weight) of both inhibitors in 250 mL of 15% HCl solution at 303 K. After establishment of the open circuit potential, potentiodynamic polarization curves were obtained with a scan rate of 0.5 mVs⁻¹ in the potential range from -700 to -300 mV with respect to the open circuit potential. The linear Tafel segments of the cathodic and anodic curves were extrapolated to the corrosion potential to obtain the corrosion current densities (i_{corr}). All potentials were measured against SCE. The percentage inhibition efficiency (η %), was calculated using the equation:

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

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

Electrochemical impedance measurements were carried out using the same electrochemical cell and electrochemical workstation as mentioned for polarization measurements in the frequency range from 100 kHz to 10 mHz, using an amplitude of 10 mV peak to peak with an ac signal at the opencircuit potential. The impedance data were obtained using Nyquist plots. The inhibition efficiency (η %) was calculated from the charge transfer resistance values obtained from impedance measurement according to the following relation:

$$\eta(\%) = \frac{R_{\rm ct\,(inh)} - R_{\rm ct}}{R_{\rm ct\,(inh)}} \times 100\tag{4}$$

where $R_{ct(inh)}$ and R_{ct} are the charge transfer resistances in the presence and absence of inhibitor respectively.

2.4.3. Scanning electron microscopic analysis

The mild steel specimens of size 1.0 cm \times 1.0 cm \times 0.1 cm were abraded with a series of emery paper (grade 320-500-800-1200) and then washed with distilled water and acetone. After immersion in 15% HCl solution in the absence and the presence of an optimum concentration of inhibitors Inh I and Inh II at 303 K for 6 h, the specimen was cleaned with distilled water, dried with a cold air blaster, and then the SEM images were recorded using JEOL JSM – 6380 LA analytical scanning electron microscope in the vacuum mode by the instrument operated at 10 kV.

2.4.4. Atomic Force Microscopy

The morphology of the uninhibited and inhibited mild steel surface was investigated by atomic force microscopy. For AFM analysis the mild steel specimens of size $1 \text{ cm} \times 1 \text{ cm} \times 0.1 \text{ cm}$ were immersed in the test solution in the absence and presence of inhibitors for 6 h at room temperature. Then the specimens were taken out from the solution, cleaned with distilled water, dried, and used for AFM. The AFM analyses were carried out using a Nanosurf Easyscan 2 instrument, Model: NT-MDT, Russia; Solver Pro-47.

2.4.5. Quantum chemical study

The quantum chemical calculations were carried out using the program package standard Gaussian 03Wsoftware with the semi-empirical AM1[19] method to calculate the physical properties of molecules. The geometries of both inhibitors were optimized by the restricted Hartree–Fock (RHF) method using the AM1 parameterization. In order to find out the none imaginary frequency which represents the minimum energy structures of inhibitors, frequency calculations were also performed along with optimization. *HOMO* and *LUMO* graphs were generated from the cube files performed in the same Gaussian suite. Results can be retrieved, viewed, and building molecular orbitals were done by GaussView (graphical interface available for Gaussian). Theoretical parameters such as the energies of the highest occupied and lowest unoccupied molecular orbitals (E_{HOMO} and E_{LUMO} , respectively), energy gap (ΔE), absolute electronegativity (χ), dipole moment (μ), global hardness (γ) and softness

(σ), molecular surface area (*SA*) and fraction of electrons transferred from the inhibitor molecule to the metal surface (ΔN) were calculated.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The values of corrosion rate and corrosion inhibition efficiency obtained from weight loss measurements for mild steel specimen immersed in 15% HCl solution in the absence and presence of different concentration of inhibitors (Inh I, Inh II) ranging from 20 to 200 ppm by weight for an immersion period of 6 h at 303 K are listed in Table 1.

Table 1. Corrosion parameters namely corrosion rate (CR), surface coverage (θ) and inhibition efficiency η (%) of mild steel in 15% HCl solution in the presence and absence of inhibitor at different temperature, obtained from weight loss measurements

Conc	e. (ppm)	303	3 K		3	13 K		323	3 K		333	3 K
	CR (mmy ⁻¹)	θ	η %	CR (mmy ⁻¹)	θ	η %	CR (mmy ⁻¹)	θ	η %	CR (mmy ⁻¹)	θ	η %
Inh I Blank 20 50	28.2 9.31 7.33	0.67 0.74	- 67.0 74.0 78.2	58.1 17.43 14.29	0.70 0.78	- 70.0 78.4	98.9 23.74 18.79	- 0.76 0.81	- 76.7 81.3	144.5 26.74 23.12	0.82 0.86	81.5 84.0
150 200	5.04 4.23	0.78 0.82 0.85	82.1 85.0	9.12 7.26 5.81	0.84 0.87 0.90	84.3 87.5 90.0	7.91 5.93	0.89 0.92 0.94	89.4 92.3 94.1	10.12 7.23	0.91 0.93 0.95	93.0 95.0
Inh II 20 50	8.14	0.71	71.1	16.27	0.72	72.4	18.79	0.81	81.4 83.9	23.12	0.84	84.0 87.0
100 150	4.51 3.10	0.84 0.89	84.0 89.0	8.13 4.65	0.80 0.86 0.92	86.6 92.5	8.90 4.96	0.83 0.91 0.94	91.2 94.2	10.12 5.78	0.93 0.96	93.0 96.0
200	2.51	0.91	91.1	4.07	0.93	93.1	4.78	0.95	95.1	5.34	0.97	96.3

3.1.1. Effect of inhibitor concentration

The corrosion inhibition efficiencies ($\eta\%$) of the inhibitors Inh I and Inh II after 6 h of immersion at 303 K as evaluated by the weight loss technique are listed in Table 1. From Table 1, it is apparent that inhibition efficiency increases with an increase in the concentration of the inhibitors. It is further evident from Table 1 that both inhibitors are good inhibitors, even at concentration as low as 20 ppm. The inhibition efficiency of Inh I and Inh II at 200 ppm was found to be 94.0% and 96.3% respectively, at 333 K (Table 1). The corrosion inhibition efficiency offered by Inh I and Inh II at lower (20 ppm) as well as higher concentration (200 ppm) was found to be better as compared to the

inhibition efficiency of most of the quinolone¹⁰⁻¹³ and thiazole¹⁴⁻¹⁶ derivatives reported in literature. The increase in inhibition efficiency with increasing concentration of inhibitors is due to an increase in the surface coverage, resulting retardation of metal dissolution [20, 21]. For inhibitor concentrations starting from 20 ppm onwards, the achieved inhibition efficiencies are above the prescribed efficiency limit for acid pickling inhibitors [22, 23]. The inhibition efficiency of Inh II is greater than Inh I at all concentrations and temperatures.

3.1.2. Effect of temperature

Corrosion inhibition studies were carried out at different temperatures ranging from 303 K to 333 K. 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 (20-200 ppm) of inhibitor at different temperatures (303 K- 333 K), obtained from weight loss measurements are shown in Table 1. It is clear from the Table 1 that the corrosion rate increases with an in the increase in temperature in the presence and absence of the inhibitors. The corrosion rate of mild steel in the absence of inhibitors increased steeply from 303-333 K whereas the corrosion rate increases slowly in the presence of inhibitors [24]. The inhibition efficiency increased with increasing temperature from 303-333 K. Such type of behaviour can be described on the basis that the increase in temperature leads to a shift of the equilibrium constant towards adsorption of the inhibitors molecules at the surface of mild steel [25].

3.1.3. Thermodynamic and activation parameters

The apparent activation energy (E_a) for dissolution of mild steel in 15% HCl can be expressed using the Arrhenius equation:

$$\log CR = \frac{-E_a}{2.303RT} + \log A \tag{5}$$

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.





Figure 2. Arrhenius plots of log *CR* versus 1000/*T* for mild steel corrosion in 15% HCl solution (a) Inh II (b) Inh I.

Figures 2 (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 Inh I and Inh II at concentrations ranging from 20 to 200 ppm.

From Figure 2, the slope of each individual line was determined, and the activation energy was calculated using the expression $E_a = (\text{slope}) \times 2.303R$. The calculated values of E_a are summarized in Table 2.

Inhibitor	Concentration (ppm)	E _a (kJmol ⁻¹)	ΔH^{*} (kJ mol ⁻¹)	$\frac{\Delta S}{(\text{Jmol}^{-1}\text{K}^{-1})}$	$Q_{ m ads}$ (kJ mol ⁻¹)
Blank	-	85.1	82.3	-36.3	
	20	70.2	65.2	-41.1	24.3
Inh II	50	64.2	62.3	-46.2	26.8
	100	60.3	60.8	-48.1	28.4
	150	61.8	59.1	-56.2	30.9
	200	60.8	58.4	-62.4	32.1
Inh I	20	72.3	71.3	-38.7	22.7
	50	70.8	68.1	-44.3	25.1
	100	68.4	66.6	-46.7	27.2
	150	66.1	64.1	-48.7	29.5
	200	64.2	62.4	-52.3	31.2

Table 2. Activation parameter for mild steel in 15% HCl solution in the absence and presence of inhibitor obtained from weight loss measurements.

Inspection of results shows that values of E_a obtained in the presence of both the inhibitors are lower than those obtained in the inhibitor free solutions. The lower activation energy in the presence of inhibitors has been explained in different ways in literature. Putilova showed that at higher temperatures, the surface covered by the inhibitor increases and rate determining step of the metal dissolution becomes the diffusion through the film of corrosion products and inhibitor [26]. Riggs and Hurd consider the rate of metal dissolution as a sum of two corrosion rates – corrosion rate of the bare metal surface and corrosion rate on the surface which is covered by adsorbed inhibitor [27]. At high degrees of coverage, the first process has no substantial contribution and the corrosive mechanism includes a direct reaction of the molecules of the inhibitor with the metal surface and the activation energy may be smaller or higher than in absence of inhibitor. According to other authors [28-31] the lower activation energy in the presence of inhibitor is indication for its chemisorption.

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

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$
(6)

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

A plot of log (*CR/T*) against 1/T (Figures 3 a, b) gave straight lines with a slope of $-\Delta H$ */2.303*R* 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 positive sign of the enthalpy reflects the endothermic nature of the mild steel dissolution process [32, 33]. 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 [34].





Figure 3. Transition state plot of log CR / T versus 1000/T for mild steel in 15% HCl solution at different concentrations (a) Inh II (b) Inh I.

3.2. Adsorption isotherm

Basic information on the interaction between the organic inhibitors and the mild steel surface are obtained from various adsorption isotherms. The surface coverage (θ) for different concentrations of inhibitors at different temperatures in 15% hydrochloric acid was tested graphically for fitting a suitable adsorption isotherm. The surface coverage area (θ) was calculated by the method described elsewhere [35].





Figure 4. Langmuir plots of (C_{inh}/θ) versus C_{inh} for (a) Inh II (b) Inh I.

Table 3. Adsorption parameters for Inh I and Inh II calculated from Langmuir adsorption isotherm formild steel in 15% HCl solution at a temperature range of 303-333 K .

Inhibitor	Temperature (K)	$K_{ m ads}$ (M ⁻¹)	$\Delta G^{\circ}_{ m ads}$ (kJ mol ⁻¹)	Correlation coefficient (R^2)	Slope values
Inh I	303	5.05×10^4	-37.3	0.992	0.97
	313	6.75×10^4	-39.3	0.996	098
	323	8.41×10^4	-41.2	0.998	0.99
	333	3.78×10^{5}	-46.6	0.999	1.02
Inh II	303	8.21×10^4	-38.6	0.996	0.97
	313	9.24×10^4	-40.2	0.997	0.98
	323	3.16×10^5	-44.7	0.998	0.99
	333	9.12×10^5	-49.1	0.999	1.01

The plots of C_{inh}/θ vs. C_{inh} for Inh I and Inh II at different temperatures yielded straight lines [Figures 4 a, b], the correlation coefficients (R^2) and slope values for lines were found in the range of 0.992 to 0.999 and 0.97 to 1.01 respectively, as listed in Table 3. The correlation coefficient and slope values in Table 3 are close to unity, indicating that the adsorption of these inhibitors on mild steel surface obey the Langmuir adsorption isotherm represented by the following equation:

$$\frac{C_{\rm inh}}{\theta} = \frac{1}{K_{\rm ads}} + C_{\rm inh}$$
⁽⁷⁾

where C_{inh} is the inhibitor concentration, K_{ads} is the equilibrium constant for adsorptiondesorption process. From the intercept of Figure 4 the values of K_{ads} were calculated. Large values of K_{ads} obtained for both the studied inhibitors imply more efficient adsorption and hence better corrosion inhibition efficiency. Using the values of K_{ads} the values of ΔG^0_{ads} was evaluated by using the following equation:

$$\Delta G_{\rm ads}^0 = -RT \ln \left(55.5 K_{\rm ads} \right) \tag{8}$$

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^0_{ads} are listed in Table 3. In general, values of ΔG^0_{ads} by -20 kJmol⁻¹ are compatible with the electrostatic interaction between the charged molecules and the charged metal (physisorption) and those which are more negative than -40 kJmol⁻¹ involve charge sharing or charge transfer from the inhibitor molecules to the metal surface (chemisorptions) [36]. The calculated ΔG^0_{ads} values for Inh I and Inh II was found in the range of -37.3 to -46.6 and -38.6 to -49.1 kJ mol⁻¹, respectively at various temperature ranges (303 K-333 K), indicates that the adsorption process of inhibitors at the mild steel surface involve chemical adsorption.

3.3. Electrochemical Studies

3.3.1. Polarization studies

The potentiodynamic polarization curves for the mild steel in 15% HCl solution in the absence and presence of different concentrations of Inh I and Inh II are shown in Figures 5 (a, b) at 303 K.





Figure 5. Potentiodynamic polarization curves for mild steel in 15% HCl solution in the presence and absence of inhibitor 303 K (a) Inh I (b) Inh II.

It is apparent from the Figures 5 (a, b), that the nature of the polarization curves remain the same in the absence and presence of inhibitors, but the curves are shifted towards lower current density in the presence of inhibitors indicating that the inhibitor molecules retard the corrosion process. The corrosion current densities and corrosion potentials were calculated by extrapolation of linear parts of anodic and cathodic curves to the point of intersection.

Table	4.	Electrochemical	parameter	and	percentage	Inhibition	efficiency	(η	%)	obtained	from
	pola	arisation studies for	or mild steel	l in 1	5% HCl solu	ution in the	presence of	r abs	ence	e of inhib	itor at
	303	К.									

Inhibitor	Concentration (ppm)	E _{corr} (mV vs SCE)	β_a (mV dec ⁻¹)	$\beta_{\rm c}$ (mV dec ⁻¹)	i _{corr} (μAcm ⁻²)	η %
Blank	-	-502	95	140	573	-
	20	-505	85	132	172	69.9
Inh I	50	-510	81	128	131	77.1
	100	-490	78	124	114	80.1
	150	-515	74	122	84	85.3
	200	-520	71	121	68	88.1
Inh II	20	-490	88	136	154	73.1
	50	-495	84	132	113	80.2
	100	-510	82	128	74	87.1
	150	-505	80	126	45	92.1
	200	-508	77	124	34	94.1

The corrosion parameters such as corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion current density (i_{corr}) and percentage inhibition efficiency (η %) obtained from these curves are given in Table 4.

The results reveal that increasing concentration of both inhibitors resulted in a decrease in corrosion current densities and an increase in inhibition efficiency (η %), suggesting the adsorption of inhibitor molecules at the surface of mild steel to form a protective film on mild steel surface [37]. The presence of inhibitors causes a minor change in E_{corr} values with respect to the value in the absence of inhibitor. This implies that the inhibitor acts as a mixed type inhibitor, affecting both anodic and cathodic reactions [38]. If the displacement in E_{corr} is more than ±85 mV vs SCE relating to corrosion potential of the blank, the inhibitor can be considered as a cathodic or anodic type [39]. If the change in E_{corr} is less than 85 mV vs SCE, the corrosion inhibitor may be regarded as a mixed type. The maximum displacement in our study was 18 mV vs SCE which indicates that Inh I and Inh II act as mixed type inhibitors. The change in the values of β_c in the presence of inhibitors clearly indicates the effect of the inhibitors on the kinetics of hydrogen evolution. The shift in the anodic Tafel slope (β_a) values may be due to the adsorption of chloride ions/or inhibitor molecules onto the mild steel surface [40].

3.3.2. EIS studies

The Nyquist plots for various concentrations of Inh I and Inh II are shown in Figures 6 (a, b).



Figure 6. Nyquist plot for mild steel in 15% HCl acid containing various concentrations of (a) Inh I (b) Inh II. (1) 0 ppm (2) 20 ppm (3) 50 ppm (4) 100 ppm (5) 150 ppm and (6) 200 ppm at 303 K.

It is clear from these plots that the impedance response of mild steel has significantly changed after the addition of inhibitors in the corrosive media. It can be seen from Figures 6 (a, b) that the Nyquist plots contains a single capacitive loop, the size of which increased by increasing the concentration of inhibitors which indicated that the impedance of an inhibited substrate increases with increasing concentration of inhibitor in 15% HCl solution. The presence of inhibitor introduces the diffusion step in the corrosion process and the reaction becomes diffusion-controlled. In the presence of inhibitors the corrosion process can have two steps in any electrochemical process at the

electrochemical interface; first, the oxidation of the metal (charge transfer process) and second, the diffusion of the metallic ions from the metal surface to the solution (mass transport process). Inhibitor gets adsorbed on the electrode surface and thereby produces a barrier for the metal to diffuse out to the bulk and this barrier increases with increasing the inhibitor concentration causing inhibition of corrosion process.

The best fitting of experimental data is represented by the Randles equivalent circuit (Figure 7), which is a parallel combination of the charge-transfer resistance (R_{ct}) and the constant phase element (CPE), both in series with the solution resistance (R_s).



Figure 7. Equivalent circuit diagram

As can be seen from Figures 6 (a, b), the Nyquist plots contain depressed semicircles with the centre under the real axis. Such behaviour is characteristic for solid electrodes and often referred to frequency dispersion, could be attributed to different physical phenomena such as roughness and in homogeneities of the solid surfaces, impurities, grain boundaries and distribution of the surface active sites [41].

Table 5. Electrochemical impedance parameters and percentage inhibition efficiency for mild steel in15% HCl solution in the absence and presence of inhibitor at different concentration at 303 K.

Inhibitor	Concentration (ppm by weight)	R_{ct} ($\Omega m cm^2$)	$\begin{array}{c} Y_0 \\ (\mu F \text{ cm}^2 \end{array}$	n	C_{dl} ($\mu \mathrm{F}~\mathrm{cm}^2$)	η %
Blank	-	25	571	0.83	245	
	20	78	514	0.71	1140	68.3
Inh I	50	102	238	0.84	117	75.5
	100	114	156	0.86	84	78.2
	150	149	104	0.91	68	83.3
	200	192	93	0.92	63	87.1
Inh II	20	90	261	0.76	80	72.4
	50	116	169	0.79	62	78.6
	100	166	97	0.86	50	85.2
	150	250	58	0.91	38	90.4
	200	312	42	0.93	30	92.1

Therefore, a constant phase element (CPE) was introduced in the circuit instead of a pure double layer capacitor (C_{dl}) to give a more accurate fit of experimental data. The impedance function of a CPE is defined by the mathematical expression given below [42]:

$$Z_{\rm CPE} = [Y_0(j\omega)^n]^{-1}$$
 (9)

where Y_0 is the magnitude of the CPE, n is the CPE exponent (phase shift), j is the imaginary number (j²= -1) and ω is the angular frequency ($\omega = 2\pi f_{max}$) for which the imaginary component of impedance is maximum. When the value of n is 1, the CPE behaves like an ideal double-layer capacitance (C_{dl}).

The impedance data such as solution resistance (R_s), charge transfer resistance (R_{ct}) and CPE constants Y₀ and n obtained from fitted spectra are listed in Table 5.

The values of the double layer capacitance (C_{dl}) were calculated from charge transfer resistance and CPE parameter values Y_0 and n using the expression [43]:

 $C_{\rm dl} = (\mathbf{Y}_0 R_{\rm ct}^{1-n})^{1/n} \qquad (10)$

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

The data of Table 5 showed that the R_{ct} values increased with increasing inhibitor concentrations suggesting the formation of a protective layer on the electrode surface. This layer makes a barrier for mass and charge-transfer at the surface of the electrode. On the other hand, the values of C_{dl} decreased with increasing inhibitor concentration, which is probably due to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor strongly adsorbed to the surface of steel [44].

Electrochemical results (η %), are in good in agreement with the weight loss experiments (η %). However, a small difference has been observed between chemical (weight loss measurements) and electrochemical measurements, which can be attributed as the chemically determined corrosion rate which is deduced from chemical dissolution process was independent of potential, whereas electrochemical measurements depend on operational potential [45].

3.4. Scanning electron microscopy

The surface morphology of the mild steel samples in 15% HCl solution in the absence and in the presence of 200 ppm of Inh I and Inh II are shown in Figures 8 (a, b c, d).

The badly damaged surface obtained when the metal was kept immersed in 15% HCl solution for 6 h without inhibitor indicates significant corrosion. However, in the presence of inhibitors the surface has remarkably improved with respect to its smoothness indicating a considerable reduction of the corrosion rate. This improvement in surface morphology is due to the formation of a good protective film of inhibitor on the mild steel surface which is responsible for inhibition of corrosion.



Figure 8. 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 inhibitor Inh II (d) with inhibitor Inh I.

3.5. Atomic force microscopy

Surface morphology of the polished mild steel and mild steel in 15% HCl solution in the absence and presence of inhibitors were investigated through atomic force microscopy (AFM). The results are shown in Figures 9 (a–d).



Figure 9. AFM micrograph of mild steel surface (a) polished mild steel (b) Blank in 15 % HCl solution (c) with 200 ppm Inh II (d) with 200 ppm Inh I.

The average roughness of the polished mild steel (Figure 8 a) and mild steel in 15% HCl solution without inhibitor (Figure 9 b) was found as 25 and 650 nm. It is clearly shown in Figure 9 (b) that the mild steel sample is getting damaged due to the acid attack on the mild steel surface. However, in the presence of an optimum concentration (200 ppm) of Inh II and Inh I as shown in Figures 9 (c, d), the average roughness were reduced to 65 and 85 nm, respectively. The lowest value of calculated roughness for Inh II reveals that Inh II protects the mild steel surface more efficiently than Inh I in 15% HCl solution.

3.6. Theoretical calculation

In order to study the effect of molecular structure on the inhibition efficiency, quantum chemical calculations were performed using semi-empirical AM1 method and all the calculations were carried out with the help of complete geometry optimization. Optimized structure, E_{HOMO} and E_{LUMO} are shown in Figure 10.



Figure 10. The optimized structure (left) and *HOMO* (center) and *LUMO* (right) distribution for molecules (a) Inh I, (b) Inh II [H, Grey; C, Cyan; N, Blue; O, Red; S, Yellow].

The E_{HOMO} is often associated with the electron donating ability of a molecule. The inhibition efficiency increases with increasing E_{HOMO} , values. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. The lower value of E_{LUMO} , suggesting that the molecule easily accepts electrons from the donor molecules [46]. It was reported previously by some researchers that smaller values of ΔE and

higher values of dipole moment (μ) are responsible for enhancement of inhibition efficiency [47]. According to HSAB theory, hard acids prefer to co-ordinate to hard bases and soft acid to soft bases. Fe is considered as soft acid and will co-ordinate to molecule having maximum softness and small energy gap ($\Delta E = E_{LUMO}$ - E_{HOMO}). The quantum chemical parameters were calculated and summarized in Table 6.

Table 6.	Quantum chemica	l parameters for	different i	inhibitors
----------	-----------------	------------------	-------------	------------

Inhibitor	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	μ (D)	γ (eV)	σ (eV ⁻¹)	ΔN	χ (eV)	<i>S.A</i> (Å ²)
Inh I	-8.181	-1.177	7.004	9.921	3.502	$0.285 \\ 0.288$	0.331	4.678	414
Inh II	-8.141	-1.191	6.951	10.989	3.475		0.336	4.665	445

For the calculations of quantum chemical parameters the following equations were used [48].

$$\chi = -\frac{E_{LUMO} + E_{HOMO}}{2}$$
(11)
$$\gamma = \frac{E_{LUMO} - E_{HOMO}}{2}$$
(12)

The inverse of the global hardness is designated as the softness, σ as follows:

$$\sigma = \frac{1}{\gamma} \tag{13}$$

where, hardness and softness measures the stability and reactivity of a molecule. Soft molecules are considered to be more reactive than hard ones because they can offer electrons to acceptors easily. For the simplest transfer of electrons, adsorption could occur at the part of the molecule where σ which is a local property, has the highest value [49].

Kokalj recently reported [50] that the work function (Φ) of a metal surface is an appropriate measure of its electronegativity and should be used together with its vanishing absolute hardness, to estimate the fraction of electrons transferred (ΔN) as

$$\Delta N = \frac{\chi_{\rm Fe} - \chi_{\rm inh}}{2(\gamma_{\rm Fe} + \gamma_{\rm inh})} = \frac{\Phi - \chi_{\rm inh}}{2\gamma_{\rm inh}}$$
(14)

where a theoretical value of $\chi_{Fe} \approx 7 \text{ eV}$ [51] is taken for iron and $\gamma_{Fe} = 0$ is taken assuming that *I*=*A* for bulk metals [52].

The theoretical studies show that the higher value of highly occupied molecular orbital energy (E_{HOMO}), number of transferred electrons (Δ N), dipole moment (μ) and softness (σ) for Inh II (Table 6) as compared to Inh I suggesting better corrosion inhibition property of Inh II as compared to Inh I. Dipole moment values of Inh I and Inh II are 9.921 D and 10.989 D respectively, which clearly

suggest that inhibitors are polar compounds and can easily donate electrons forming strong $d\pi$ - $p\pi$ bonding [53]. In the present study the inhibition efficiency increases with the increasing dipole moment of the inhibitors, which could be attributed as higher polarity compounds will facilitate electrostatic interaction between the electric field due to the charged metal surface and electric moments of the inhibitors and contributes to their better adsorption by influencing the transport process through the adsorbed layer [54]. The inhibitor Inh II, which has the highest value of σ (0.288 eV⁻¹), has the highest efficiency (Table 6). According to the Lukovits study [55], if the value of ΔN is < 3.6, the efficiency of inhibition increases with increasing electron donating ability of the inhibitor at the metal surface. Higher values of ΔN indicating the good performance of the inhibitors. Thus, the presence of an electron donating substituent $-OCH_3$ in Inh II increases its inhibition efficiency. It has been found that the large surface area values obtained for both studied inhibitors (Table 6) attributed to the uniformity of coverage of the surface of the mild steel.

Figure 9, reveals that the *HOMO* and *LUMO* location in both inhibitors is mostly distributed in vicinity of the nitrogen and sulfur atoms of the thiazole ring, C=N group and phenyl ring attached to C=N group. These indicate the reactive sites for the interaction between inhibitor molecules and mild steel surface.

3.7. Mechanism of inhibition

Corrosion inhibition of mild steel in hydrochloric acid solution by different inhibitors (Inh I and Inh II) 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 and sulfur 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 quinoline ring, thiazole ring, phenyl ring and lone pair of electrons of nitrogen, sulfur and oxygen atoms present in both the inhibitors which decrease the anodic dissolution of mild steel.

The inhibitors Inh I and Inh II are expected to get adsorbed through the lone pairs of electrons on N and sulfur atoms of thiazole ring, -C=N group, N-H group, -C=O group and delocalized π -electron density on the thiazole and phenyl rings by their coordination with mild steel surface.

4. CONCLUSIONS

The effect of electrochemical and quantum chemical studies on adsorption and corrosion inhibition performance of quinoline-thiazole derivatives on mild steel in hydrochloric acid solution were investigated. The following conclusions were drawn:

The synthesized quinoline-thiazole derivatives show good inhibition efficiencies for the corrosion of mild steel in 15% HCl solutions and the inhibition efficiency increases on increasing the

concentration of these inhibitors and increase in temperature. The inhibiting performance of Inh II is better than Inh I.

EIS measurements show that charge transfer resistance (R_{ct}) increases and double layer capacitance (C_{dl}) decreases in presence of inhibitors, suggested the adsorption of the inhibitor molecules on the surface of mild steel.

> It is suggested from the results obtained from SEM and Langmuir adsorption isotherm that the mechanism of corrosion inhibition is occurring mainly through adsorption process.

 \triangleright Quantum chemical results of Inh I and Inh II show higher value of E_{HOMO} , lower value of E_{LUMO} , and smaller value of ΔE , indicating that these inhibitors are good corrosion inhibitor for mild steel in hydrochloric acid.

ACKNOWLEDGEMENTS

The authors acknowledge University of KwaZulu-Natal for a postdoctoral scholarship for Dr I. Bahadur.

References

- 1. W. Li, Q. He, C. Pei, B. Hou, *Electrochim. Acta*, 52 (2007) 6386–6394.
- 2. Q. Zhang, Y. Hua, *Electrochim. Acta*, 54 (2009) 1881–1887.
- 3. A. Döner, R. Solmaz, M. Özcan, G. Kardaş, Corros. Sci., 53 (2009) 2902–2913.
- 4. M. Yadav, U. Sharma, J. Mater. Environ. Sci., 2 (2011) 407–414.
- 5. M. M. Singh, S. Banerjee, V. Srivastava, Corros. Sci., 59 (2012) 35-41.
- 6. M. Yadav, D. Behera, U. Sharma, Arab. J. Chem. doi: 10.1016/j.arabjc., 2012.03.011
- 7. M. Yadav, D. Behera, S. Kumar, R.R. Sinha, Ind. Eng. Chem. Res., 52 (2013) 6318–6328.
- 8. M. Yadav, D. Behera, U. Sharma, Corros. Eng. Sci. Technol., 48 (2013) 19–27.
- 9. R. Solmaz, G. Kardaş, M. Çulha, B. Yazıcı, M. Erbil, *Electrochim. Acta*, 53 (2008) 5941–595.
- 10. M.S. Abdel-Aal, M.S. Morad, Br. Corros. J., 36 (2001) 253-260.
- 11. G. Achary, H.P. Sachin, N.Y. Arthoba, T.V. Venkatesha, Mater. Chem. Phys., 107 (2008)_44-50.
- 12. E.E. Ebenso, I.B. Obot, L.C. Murulana, Int. J. Electrochem. Sci., 5 (2010)1574-1586.
- 13. B. M. Mistry, N. S. Patel, S. Sahoo, S. Jauhari, Bull. Mater. Sci., 35 (2012) 459-469.
- 14. M.A. Quraishi, H.K. Sharma, J. Appl. Electrochem., 35 (2005) 33-39.
- 15. A.A. Al-Sarawya, A.S. Fouda, W.A.S. El-Deina, Desalination, 229 (2008) 279–293.
- 16. K.F. Khaled, M.A. Amin, Corrosion Science, 51 (2009) 1964–1975.
- 17. N.C. Desai, N. Shihory, K. Rajpara, A. Dodiya, Indian J. Chem., 51B (2012) 508-513.
- 18. A. Dhanapala, S.R. Boopathy, V. Balasubramanian, J. Alloys Comp., 523 (2012) 49-60.
- 19. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc., 107 (1985) 3902-3909.
- 20. S.S. Abdel-Rehim, A.M.I. Magdy, K.F. Khaled, J. Appl. Electrochem., 29 (1999) 593–599.
- 21. A.U. Ezeoke, O.G. Adeyemi, O.A. Akerele, N.O. Obi-Egbedi, Int. J. Electrochem. Sci., 7 (2012) 534–553.
- 22. A. Popova, Corros. Sci., 49 (2007) 2144–2158.
- 23. H. Keleş, M. Keleş, I. Dehri, O. Serindağ, Colloids Surf. A, 320 (2008) 138-145.
- 24. E.E. Ebenso, I.B. Obot, Int. J. Electrochem. Sci., 5 (2010) 2012–2035.
- 25. 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.

- 26. L.N. Putilova, S.A. Balezin, V.P. Barannik, *Metallic Corrosion Inhibitors, Pergamon Press, NY*, 1960.
- 27. O.L. Riggs, R.M. Hurd, Corrosion, 23 (1967) 252-260.
- 28. F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin, M. Lagrenée, *Corros. Sci.*, 44 (2002) 2271–2289.
- 29. S.A. Umoren, I.O. Igwe, E.E. Ebenso, Corros. Sci., 50 (2008) 1998–2006.
- 30. A.R.S. Priya, V.S. Muralidharam, A. Subramania, Corrosion, 64 (2008) 541–552.
- M.A. Amin, M.A. Ahmed, H.A. Arida, T. Arslan, M. Saracoglu, F. Kandemirli, Corros. Sci., 53 (2011) 540–548.
- 32. G. Quartarone, G. Moretti, A. Tassan, A. Zingales, Mater. Corros., 54 (1994) 641-647.
- K. T. Emranuzzaman, S. Vishwanathan, G. Udaybhanu, *Corros. Eng. Sci. Technol.*, 39 (2004) 327– 332.
- 34. S.V. Ramesh, V. Adhikari, Bull. Mater. Sci., 31 (2007) 699-711.
- 35. S.M. Mayanna, J. Electrochem. Soc., 122 (1975) 251-252.
- 36. M. Behpour, S.M. Ghoreishi, N. Soltani, M. Salavati-Niasari, M. Hamadanian, A. Gandomi, *Corros. Sci.*, 50 (2008) 2172–2181.
- 37. X. Wang, H. Yang, F. Wang, Corros. Sci., 53 (2011) 113-121.
- 38. D. Jayaperumal, Mater. Chem. Phys., 119 (2010) 478-484.
- 39. E.S. Ferreira, C. Giancomlli, F.C. Giacomlli, A. Spinelli, Mater. Chem. Phys., 83 (2004) 129-134.
- 40. E. McCafferty, N. Hackerman, J. Electrochem. Soc., 119 (1972) 146-154.
- 41. M. Behpour, S.M. Ghoreishi, N. Mohammadi, N. Soltani, M. Salavati-Niasari, *Corros. Sci.*, 52 (2010) 4046–4057.
- 42. I. Ahamad, R. Prasad, M.A. Quraishi, Corros. Sci., 52 (2010) 933-942.
- 43. A.R.S. Priya, V.S. Muralidharam, A. Subramania, Corrosion, 64 (2008) 541–552.
- 44. K.F. Khaled, N. Hackerman, Mater Chem. Phys., 82 (2003) 949–960.
- 45. E.E.F. El-Sherbini, S.M.A. Wahaab, M. Deyab, Mater. Chem. Phys., 89 (2005) 183-191.
- 46. S. Xia, M. Qiu, L. Yu, F. Liu, H. Zhao, Corros. Sci., 50 (2008) 2021-2029.
- 47. Y.M. Tang, W.Z. Yang, X.S. Yin, Y. Liu, R. Wan, J.T. Wang, Mater. Chem. Phys., 116 (2009) 479-483.
- 48. R.G. Pearson, Inorg. Chem., 27 (1998) 734–740.
- 49. V.S. Sastri, J.R. Perumareddi, Corrosion, 53 (1997) 617-622.
- 50. A. Kokalj, Chem. Phys., 393 (2012) 1-12.
- 51. J.C. Slater, Introduction to Chemical Physics, Dover, New York, 1970.
- 52. M.J.S. Dewar, W. Thiel, J. Am. Chem. Soc., 99 (1977) 4899-4907.
- 53. I.B. Obot, N.O. Obi-Egbedi, Mater. Chem. Phys., 122 (2010) 325-328.
- 54. K. Babić-Samardžija, K.F. Khaled, N. Hackerman, Appl. Surf. Sci., 240 (2005) 327-340.
- 55. I. Lukovits, E. Klaman, F. Zucchi, Corrosion, 57 (2001) 3-8.

© 2014 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).