Int. J. Chem. Sci.: 13(4), 2015, 1693-1704
ISSN 0972-768X
www.sadgurupublications.com

CORROSION INHIBITION AND QUANTUM MECHANICAL STUDIES OF L80 CARBON STEEL IN KHUFF GAS ENVIRONMENT- A LABORATORY SCALE STUDY

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ABSTRACT

The corrosion inhibition of L80 carbon steel sheets in Khuff gas well environment with sulfisoxazole (SZ) as green inhibitor has been evaluated by mass loss, potentiodynamic polarization, electrochemical impedance spectroscopy and quantum mechanical studies. All these techniques reveal that the SZ inhibits the corrosion of L80 carbon steel in acidified H_2S/CO_2 environment. Polarization studies indicated that inhibitor is acted as mixed type. The adsorption of the compounds on L80 carbon steel surface follows Langmuir adsorption isotherm.

Key words: Antibiotics, Hydrogen permeation, Corrosion inhibitors, Green inhibition.

INTRODUCTION

L80 is a medium carbon steel most commonly used in downhole equipment such as Khuff gas wells[1-4]. The Khuff gases produce H_2S/CO_2 in various ratios in which H_2S gas adsorbs on steel surface by forming iron sulfide as barrier, which prevents localized corrosion attack on steel in acidified environment. However, many cases of failure of L80 carbon steel pipes and tanks have been investigated due to corrosion processes in acidified environment, which was evidently proved by the formation of rust in those systems that leads to severe damage to L80 carbon steel[5-7].

Several methods were used to retard the dissolution of metals in acidic medium, but the use of inhibitors is most commonly used[8-10].

The usage of inhibitors is cheap and real method to retard electrochemical corrosion. Numerous organic compounds, which contain π bonds and hetero atoms such as sulphur,

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nitrogen, oxygen and phosphorous allow the adsorption of compounds on the carbon steel surface were reported as corrosion inhibitors by several investigators[11-16] for dissolution of medium carbon steel in acid medium. Research findings in recent times are stimulated towards emerging the cheap, and non-toxic drugs as environment responsive corrosion inhibitors[17-24].

The literature review demonstrates that few antibiotics have been reported as corrosion inhibitors for the corrosion of steel and aluminium in acidic and alkaline media[25]. Recently, Hari Kumar and Karthikeyan[26] used torsemide drug as inhibitor for the corrosion of mild steel in 1 M HCl. Nevertheless, no concrete reports have been published for the corrosion inhibition of L80 carbon steel in acidified H_2S/CO_2 environment with use of sulfisoxazole (SZ) as as inhibitor and hence, the present study.

The inhibition performance of the compound was monitored using mass loss and electrochemical techniques. Seldom, the usage of hydrogen permeation measurement studies for this green inhibitor established the prominent performance of this compound in acidified sour gas environment. This inhibitor is big enough, amply planar and could be able to block more L80 carbon steel surface area.

EXPERIMENTAL

Materials

L80 carbon steel specimens of size 1 × 4 cm^2 were used for mass loss and electrochemical studies. The aggressive solution of 5% NaCl (AR Grade) is used for all the studies. The antibiotic namely sulfisoxazole (SZ) was procured from the medicine shop and used as such without further purification. The structure of the green inhibitor is given in the Fig. 1, which also includes ^{13}C-NMR shifts. Electrochemical experiments were performed with a three electrode cell assembly with L80 carbon steel samples as working electrode, platinum as counter electrode and saturated calomel (SCE) as the reference electrode.

Mass loss studies

Mass loss and hydrogen permeation studies were done as described earlier[27]. The concentrations of inhibitor used for weight loss and electrochemical study were from 1 mM to 100 mM. L80 carbon sheet specimens of size 1 × 4 cm^2 were abraded with different emery papers and then degreased with acetone. The cleaned surfaces were washed with double distilled water, air dried and preserved in the desiccator. The mass loss study was followed at room temperature for three hours in Khuff gases environment. Khuff gases environment was optimized in the laboratory scale by dissolving (1:1) Na_2S and $NaHCO_3$

w/v in 10% HCl, which produce H_2S and CO_2 gases. The inhibition efficiency (IE%) was calculated by the following equation,

$$\text{Inhibition efficiency (IE\%)} = (W_a - W_p / W_a) \times 100 \qquad \ldots(1)$$

Where W_a and W_p are the weight loss values in absence and presence of the green inhibitor.

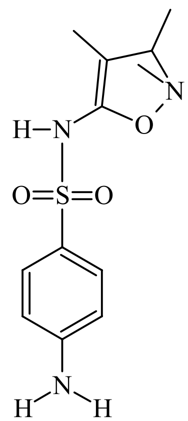

Fig. 1: Structure of sulfisoxazole

Potential-current measuremnts by electrochemical studies

Potentiodynamic polarization measurements were monitored in a conventional three electrode cylindrical glass cell, using CH electrochemical analyzer at a scan rate of 5 mV s^{-1}. Before carrying out the polarization measurements, the solution was deaerated for 20 min. and the working electrode was maintained at its corrosion potential for 20 min until a steady state was obtained. The L80 carbon steel surface was introduced into various concentrations of inhibitors in Khuff gas mixture at 60ºC. The inhibition efficiency (IE%) was calculated using the equation,

$$\text{Inhibition efficiency (IE\%)} = (I_a - I_p/I_a) \times 100 \qquad \ldots(2)$$

Where I_a and I_p are the corrosion current density without and with the green inhibitor, respectively.

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -950 mV to +100 mV versus the open circuit potential. The corresponding corrosion current (I_{corr}) was recorded. Tafel plots were made by plotting

E versus log *I*. Corrosion potential (E_{corr}), corrosion current density (I_{corr}) and cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures.

Impedance measurements were done in the frequency range from 0.1 to 10000 Hz by means of an amplitude of 20 mV and 10 mV peak to peak with an AC signal at the open-circuit potential. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were obtained from Nyquist plot[28-30]. The percentage inhibition efficiency was calculated from the equation,

$$\text{Inhibition efficiency (IE\%)} = (C_{dl}^{a} - C_{dl}^{p}/C_{dl}^{a}) \times 100 \quad \ldots(3)$$

Where $C_{dl}{}^{a}$ and $C_{dl}{}^{p}$are the charge transfer resistance of L80 carbon sheets without and with green inhibitor, respectively.

RESULTS AND DISCUSSION

Mass loss studies

The values of inhibition efficiency (IE%) and surface coverage (θ) were calculated for green inhibitor at different concentrations for the corrosion reaction of L80 carbon sheets in Khuff gas environment. The results are summarized in the Table 1. It is established that inhibition efficiency increases with increase in the inhibitor concentration. It was also ostensible that corrosion rate decreases with increase in green inhibitor concentration. It was illustrious that inhibitors retard the L80 carbon steel corrosion at all the concentrations used in the study. Maximum inhibition efficiency is observed at 100 mM concentrations of the Sulfisoxazole.

Table 1: Values of inhibition efficiency and surface coverage for the dissolution of L80 carbon steel in Khuff gas media in presence of different concentrations of sulfisoxazole obtained from mass loss measurements

Inhibitor conc.	Inhibition efficiency (*IE*) (%)	Surface coverage (θ)
Sulfisoxazole		
Blank	-	-
25 ppm	75.23	0.75
50 ppm	87.52	0.88
75 ppm	98.24	0.98

Potential-current measuremnts by electrochemical studies

Polarization results such as the values of corrosion potential (E_{corr}), corrosion current densities (I_{corr}), anodic tafel slope (β_a), cathodic tafel slope (β_c) surface coverage (θ) and inhibition efficiency (IE%) were calculated using polarization curves for the dissolution of L80 carbon sheets in Khuff gas environment are summarized in Table 2.

It can also be seen from the table that corrosion current (I_{corr}) value declines with increase in the concentration of the green inhibitor. Further it is well-known that increasing concentrations of sulfisoxazole enhance the values of both β_a and β_c, in a random manner. Hence, the inhibition of corrosion by this compound is under cathodic control, but chiefly under mixed type. The inhibition efficiency (IE%) and surface coverage (θ) increases with increase in SZ dosage in the experiment.[31,32] The maximum inhibition efficiency was obtainable at 100 ppm concentration. A definite relationship exists between the results obtained from mass loss and potential-current studies for the above inhibitor.

Table 2: Electro kinteic parameters and inhibition efficiency for corrosion of L80 carbon steel in Khuff gas environment obtained by polarization method in presence of sulfisoxazole

Inhi. conc. (ppm)	E_{corr} (mV vs SCE)	I_{corr}	βa (µA cm^{-2})	βc (mV dec^{-1})	*IE* (mV dec^{-1})	θ (%)
Blank	-857.78	647.47	100.9	150.2	-	-
25	-837.35	161.80	81.9	127.8	75.05	0.75
50	-801.63	77.89	98.8	137.9	87.86	0.88
75	-792.77	10.74	77.4	104.7	98.32	0.98

Electrochemical impedance studies

The Nyquist representations of impedance behavior of L80 carbon sheets in Khuff gas environment with and without presence of various concentrations of inhibitors are given in Table 3. The table also contained the values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) derived from Nyquist plots for the dissolution of L80 carbon sheets in Khuff gas environment. It can be visualized that the values of R_{ct} was seen to increase with increase in concentration of green compound in the acid. It was found that values of C_{dl} are brought down by enhancing concentrations of sulfisoxazole in the acid medium. This can be accredited tothe increasing adsorption of the inhibitor on the metal surface with increase in its concentration[33].

Table 3: Electrochemical impedance parameters for dissolution of L80 carbon steel in Khuff gas environment with and without SZ compound

Inhibitor conc. (ppm)	R_{ct} (Ω cm^2)	C_{dl} (F cm^{-2})	*IE* (%)	Surface coverage (*θ*)
Blank	47.2	0.296	-	-
Sulfisoxazole				
25	126.7	0.0727	75.05	0.75
50	177.6	0.0376	86.95	0.87
75	270.82	0.0048	98.34	0.98

Adsorption isotherm

The degree of surface coverage (*θ*) for different concentrations of SZ in Khuff gas environment has been calculated from weight loss, polarization and electrochemical impedance studies. The obtained data was tested graphically for fitting suitable isotherm[34-36]. A straight line was observed by plotting log (C/*θ*) Vs log C, which ratifies that the adsorption of this green inhibitor observes Langmuir adsorption isotherm.

The Langmuir isotherm for the adsorbed layers is given by the equation[37],

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad \ldots(7)$$

Where K_{ads} is the equilibrium constant of the adsorption/desorption process. Adsorption equilibrium constant (K_{ads}) and free energy of adsorption [ΔG^o_{ads}] were calculated using the equation[38].

$$K_{ads} = 1/C_{inh} \times \theta / 1-\theta \quad \ldots(8)$$

$$\Delta G^o_{ads} = -2.303RT \log [55.5K_{ads}] \quad \ldots(9)$$

Where 55.5 is the molar concentration of water in solution[38,39]. R is the gas constant, and T is the temperature. The values of adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG^o_{ads}) are given in Table 4. The negative values of (ΔG^o_{ads}) showed that adsorption of SZ on L80 steel surface in chloride environment is an extemporaneous process. It is well-known that values of (ΔG^o_{ads}) is of order 20 $kJmol^{-1}$ or lower indicates a physisorption, those of order of -40 $kJmol^{-1}$ or higher involve charge sharing or transfer from the inhibitors to the metal surface to form a coordinate bond, the process known as chemisorption. The values of free energy of adsorption (ΔG^o_{ads}) in this study lies in the range -28 to -32 $kJmol^{-1}$, demonstrating that the adsorption is not a simple physisorption but it may include some other interactions[40-43].

Table 4: Gibbs free energy parameters and adsorption equilibrium constant (K_{ads}) of green inhibitor (SZ) at different temperatures evaluated by mass loss method

Temperature [K]	K_{ads}	$-\Delta G^o_{ads}$ [$kJmol^{-1}$]
	Green inhibitor	Green inhibitor
313	932	28.31
323	1164	29.84
333	1345	31.17

Mechanism of inhibition

In sulfisoxazole, the presence of lone pairs of electrons of nitrogen atoms of both oxazole moiety, 4-amino and benzene sulphonamide groups favored the adsorption of SZ on oxidized L80 carbon steel effect by virtue of releasing electrons to the positively charged Fe atoms, when exposed to Khuff gas environment.

Quantum mechanical studies

Quantum mechanical calculations were carried out to explore the adsorption and inhibition mechanism of the SZ inhibitor on the corrosion of L80 carbon steel surfaces in Khuff gas environment. Fig. 2 & 3 indicate HOMO and LUMO structure of sulfisoxazole inhibitor. The values of calculated quantum chemical parameters i.e. E_{HOMO} (highest occupied molecular orbital), E_{LUMO} (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment) etc. are presented in Table 5. E_{HOMO} is related to the electron-releasing capability of the inhibitor molecule while E_{LUMO} is explained for electron with drawing capacity of inhibitor molecule.

Table 5: Quantum mechanical parameters for sulfisoxazole for the corrosion of GI surfaces

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE ($Cal.mol^{-1}$)	Dipole moment (Debye)
Sulfisoxazole	-0.6023	-8.1775	7.5752	3.8

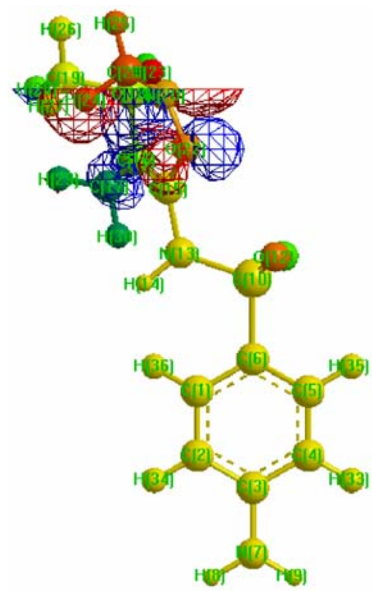

Fig. 2: Highest molecular orbital of SZ molecules during the adsorption on L80 carbon steel surfaces

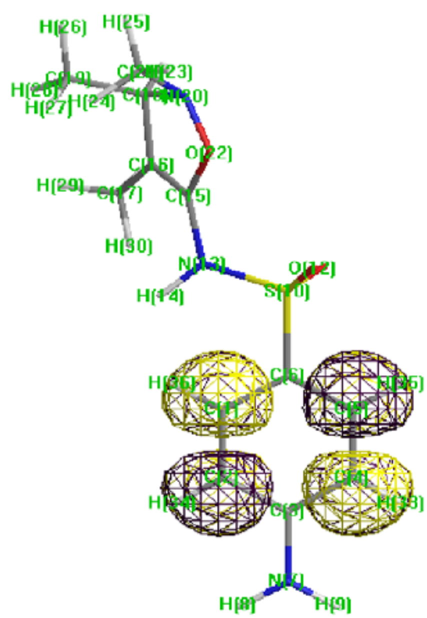

Fig. 3: Lowest unoccupied molecular orbital of SZ molecules during the adsorption on L80 carbon steel surfaces

In the present investigation, the adsorption of SZ on metal surface acquired on the basis of donor-acceptor interactions between the π-electrons of nitrogen and sulphur atoms of oxazole groups along with 3-amino and benzene sulphonamide groups, which favors effective adsorption of SZ on L80 carbon steel surfaces as evidenced from the dense electrons cloud in HOMO and LUMO structure, wherein the electroic cloud is similar in both orbitals. It is well understood that if both HOMO and LUMO structures are resembling each other, the resultant adsorption of inhibitor will be better on metal surface. The gap between HOMO–LUMO energy levels of molecules was another important factor that needs to be considered. Higher the value of ΔE of an inhibitor, higher is the inhibition efficiency of that inhibitor. It has been reported that large values of the dipole moment will improve corrosion inhibition. Based on the values of ΔE and dipole moment, the compound SZ has strongly been adsorbed on galvanized steel surface exposed in Khuff gas environment.

CONCLUSION

The controlled dissolution of L80 carbn steel surfaces were monitored and controlled in Khuff gas environment at different temperatures (313-333 *K*) without and with various concentrations of sulfisoxazole, a green inhibitor by adapting chemical and electrochemical methods. The main conclusions are:

(i) Sulfisoxazole drug exhibited inhibiting properties for galvanized steel corrosion in Khuff gas effectively.

(ii) Tafel polarization plots indicated that tested inhibitor was showing mixed mode of inhibition.

(iii) Rates of corrosion obtained from the impedance measurements were in good agreement with those recorded using the potential-current plots. This confirms the validity of the corrosion rates measured by the potentiodynamic polarization.

(iv) Adsorption of the sulfisoxazole on L80 carbon steel was found to follow Langmuir isotherm.

(v) Apparent activation energies in the presence of sulfisoxazole drug for the corrosion of low carbon steel in Khuff gas environment lie in the range 28 to -32 $kJmol^{-1}$, indicating that the adsorption is not a simple physisorption.

(vi) Quantum mechanical results validate the impressive performance of SZ inhibitor through its effective adsorption on L 80 carbon steel surfaces in Khuff gas medium.

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Revised : 22.07.2015 *Accepted : 24.07.2015*