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Quantum mechanical and hydrogen permeation studies on the corrosion of stainless steel in acid medium using a novel inhibitor

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ABSTRACT

The inhibitive action of lansoprazole (LPZ) on stainless steel 304 corrosion and permeation of hydrogen gas in 2N H_3PO_4 has been analyzed using weight loss, gasometric and electrochemical studies. The antibiotic seems to be more effective in reducing the dissolution of steel in 2N H_3PO_4 . Potential-Current curves clearly indicated that the compound observes mixed mode of inhibition in 2N H_3PO_4. Hydrogen permeation and EIS measurements have confirmed that LPZ retards the corrosion of SS 304 effectively . The quantum mechanical studies validated the performance of the inhibitor molecule through its effective adsorption on steel surfaces using theoretical values of E_{HOMO}, E_{LUMO}, ΔE and dipole moment of inhibitor .

Keywords: Corrosion, potential, hydrogen permeation, impedance, inhibition

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INTRODUCTION

In recent years , the medicines such as antibiotics and drugs are preferentially used as corrosion inhibitors due to their ecofriendliness [1-4]. Hetero cyclic compounds with sulphur, nitrogen and oxygen atoms in their exo cyclic rings have widely been reported as inhibitors for metals in acidic media [5-8]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The careful perusal on literature studies evidently disclose that no methodical approach is remaining on the inhibitive action of lansoprazole (LPZ) in high aggressive acid solutions. The lone pair of electrons on nitrogen atoms of benzimidazole and pyridine methyl sulfonyl moieties and delocalization of electrons of trifluoro ethoxy group of the present drug affluence the adsorption of the compound on surface of SS 304 . All the above research describes a general information that no significant data is seen on the performance of lansoprazole as impressive corrosion inhibitor and in reducing the entry of hydrogen gas through steel when immersed in 2N H_3PO_4 . It is a proton-pump inhibitor (PPI) which inhibits the stomach's production of gastric acids.The molecular mass of the inhibitor is 369.36 g/mol.

MATERIALS AND METHODS

Stainless steel 304 specimens of the following composition was widely used.

C= 0.08% , Si = O%, Ni = 8%, Cr = 18% and Fe= balance with exposed area of 4 x 1 x 0.020 cm were used for weight loss and hydrogen permeation measurements. A stainless steel cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.3 cm^2 was employed for potentiodynamic polarization and impedance measurements.

The compound was mainly screened by a weight loss studies as reported by Madhavan et al [9]. Both cathodic and anodic potential- current curves were measured potentiodynamically (1 mV s^{-1}) using corrosion measurement system BAS Model: 1OOA computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil of 4 cm^2, $Hg/Hg_2Cl_2/KCl_{(satd)}$ was

used as auxiliary and reference electrodes, respectively. The hydrogen permeation study was carried out using the procedure given by Devanathan and Stachurski's, as defined earlier.[9] Double layer capacitance (Cdl) and chare transfer resistance values (R,) were got using electrochemical impedance measurements .

RESULTS AND DISCUSSION

3.1 Weightloss and Gasometric studies

Table 1 gives the results of inhibition efficiency for various concentrations of lansoprazole for the corrosion of SS 304 in 2N H_3PO_4 obtained from weight loss and gasometric measurements. It is perceived that the inhibitor impedes the dissolution of stainless steel much effectively in H_3PO_4. This can be attributed to the slighter adsorption of sulphate ions on the steel surface, thereby allowing more space for the tobramycin compound to get adsorbed. In H_3PO_4, the coverage of the SS 304 by the lansoprazole is significantly larger , giving rise to higher values of inhibition action at all concentrations of the LPZ molecule. The structure of the compound is given in Figure 1.

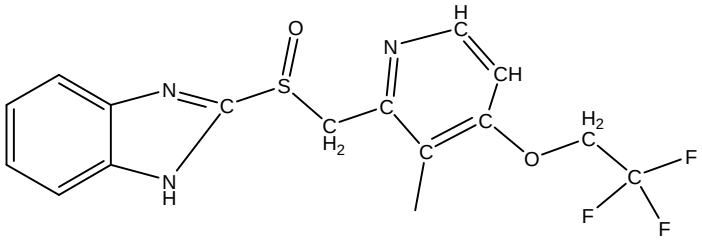

Figure 1. Structure of Lansoprazole

The retardation on the dissolution of SS 304 in acid medium favoured by Tobramycin were involving the following interactions:

1.The interaction between the lone pairs of electrons of the nitrogen atoms of benzimidazole and pyridine methyl sulfonyl groups and the positively charged metal surface [10].

2.The interactions between delocalized electrons of trifluoro ethoxy moieties and the positively charged metal surface [11].

Table 1. Values of inhibition efficiency for the corrosion of mild steel in 2N H_3PO_4 in the presence of different concentrations of lansoprazole obtained from weight loss and gasometric measurements

Concentration of Inhibitor (mM)	Inhibition efficiency (%)	
	Weight loss studies	Gasometric measurements
5	74	73.8
10	79	78.9
15	89	89.3
20	96.2	96.0

It is found that there is a very good agreement between the values of inhibition efficiency obtained by weight loss and gasometric studies.

3.2 Potentiodynamic polarization measurements

Table 2 indicated the results of corrosion kinetic factors such as Tafel slopes (b_a and b_c), corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency derived from potentiodynamic polarization studies for SS 304 in 2N H_3PO_4 containing different concentrations of lansoprazole molecule. It can be envisaged from this table that results of Tafel slopes and I_{corr} are very much similar to those reported earlier [12,13.] Further it is recognized that increasing concentrations of green inhibitor increases the values of both b_a and b_c in random fashion justifying that the inhibition of corrosion of SS 304 in 2N H_3PO_4 follows mixed mode of reaction. Values of E_{corr} is shifted to positive direction in the presence of various concentrations of LPZ molecule. This can be accredited to the formation of sturdily adsorbed inhibitor film on the SS 304 surface. The presence of increasing dosage of inhibitor ominously retards I_{corr} values in both the acids. It can also be observed that most of the values of inhibition efficiency obtained by weight loss and potentiodynamic polarization studies agree very well.

Table 2. Corrosion kinetic parameters of SS 304 in 2N H_3PO_4 in the presence of different concentrations of Lansoprazole obtained from potentiodynamic polarization studies

Concentration of Inhibitor (mM)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} mA cm^{-1}	Inhibition efficiency (%)	
		b_a	b_c			
Blank	-912	74	132	264	---	
10	-881	72	144	68.64	74	
20	-870	76	135	55.44	79	
35	-862	60	157	29.04	89	
40	-857	54	137	10.03	96.1	

3.3 Hydrogen permeation studies

The outcomes of hydrogen permeation measurements for the corrosion of stainless steel 304 in the presence and absence of the LPZ molecule are given in Table 3.Hydrogen permeation currents for mild steel in acid medium is more, because of the highly reactive nature of phosphate ions. It can be obtained from the table that the existence of inhibitor in acid medium reduces the permeation current and does not favour the entry of hydrogen gas into SS 304 . The declining trend in permeation currents can be attributed to the presence of strong protective layer by green inhibitor on the surface of SS 304 [14,15] . It can be visualized from the table that the decrement of permeation current is more, if the concentration of lansoprazole is more.

Table 3. Values of permeation current for the corrosion of SS 304 in 2N H_3PO_4 in the presence of different concentrations of Lanzoprazole

Concentration of Inhibitor (mM)	Permeation current (A X 10^{-6})
	1M H_3PO_4
Blank	19.7
10	16.2
20	13.4
30	11.4
40	7.1

3.4 Impedance measurements

Values of charge transfer resistance (R_t)and double layer capacitance (C_{dl}) obtained from EIS measurements are given in table 4. It can be noticed that the values of R_t is begun to increase with enhancement of LPZ concentrations in acid medium . Values of double layer capacitance are confirming that steel dissolution of SS 304 can be controlled in the presence of inhibitor molecule in 2N H_3PO_4 .It is noticed that values of C_{dl} are brought down by increasing concentrations of LPZ in acid medium. This can be ascribed to the remarkable adsorption of the antibiotic molecule on the surface of SS 304 with increase in its dosage to the corrosive medium.

Table 4.Impedance parameters for the corrosion of Stainless steel 304 in 2N HCl and 2N H_3PO_4 in the presence of different concentrations of Clotrimazole

Concentration of Inhibitor (mM)	2N H_3PO_4	
	Charge Transfer resistance (R_t) ($Ohm.cm^2$)	Double layer capacitance (C_{dl}) ($\mu F.cm^{-2}$)
Blank	6.99	184.4
5	49.20	48.24
10	60.23	38.72
15	77.42	20,28
20	135.31	7.01

A plot of surface coverage (ø) versus log C gave a straight line signifying that the adsorption of lansoprazole on SS 304 surface in 2N H_3PO_4 obeys Temkin's adsorption isotherm [16]. This is a principal support to corrosion inhibition by this molecule , as a consequence of its adsorption on the surface of SS 304.

3.5 Quantum mechanical studies:

The computed quantum mechanical indices such as energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), LUMO- HOMO, energy gap (ΔE), dipole moment (μ), are given in Table 5. From figure 2 and 3 , it can be observed that HOMO and LUMO energy orbital's were stalwartly distributed on benzimidazole and methyl sulfoxide groups for HOMO and LUMO structures launching that the lansoprazole has good adsorption sites [17–19] and this is in agreement with publications of molecular orbital studies antagonizing that π electrons and N atoms are responsible for inhibition activity[20].

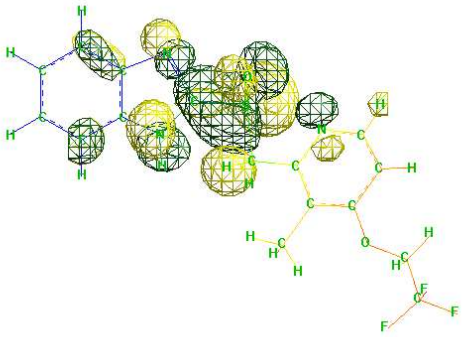

Figure 2. Highly Occupied MO's of LPZ

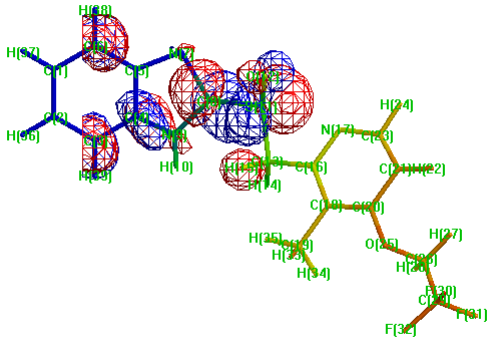

Figure 3. Lowest unoccupied MO's of LPZ

Table 5: Quantum chemical parameters for Lansoprazole inhibitor

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Lansoprazole	-2.6652	-7.01439	4.34	3.7

It has been widely reported that, higher the value of E_{HOMO}, larger is the easiness for an inhibitor to donate electrons to vacant d orbital of Fe atom and higher is its adsorption [21]. Also, lower E_{LUMO} values , favours acquiring capacity of electrons by the inhibitor from Fe atom to form feedback bonds. Hence the gap between HOMO–LUMO energy levels of molecules was considered as an important data . Smaller the value of ΔE of an inhibitor, greater is the inhibition efficiency of that compound . It is further reported that, large values of dipole moment will substantially raise the adsorption of the inhibitor on metal surface [22-24].

CONCLUSION

1. Lansoprazole reduces the dissolution of the corrosion of SS 304 in both acids, but shows a better performance in 2N $H3PO_4$.
2. The inhibition of corrosion of stainless steel by the green molecule in H_3PO_4 falls under mixed control.
3. The presence of inhibitor molecule in 2N $H3PO_4$ is found to diminish the degree of hydrogen permeation current through SS 304 surface.
4. R_t and C_{dl} values studied from impedance measurements justify the impressive performance of the lansoprazole compound.
5. The adsorption of the compound on SS 304 surface follows Temkin's adsorption isotherm which is further validated by quantum mechanical values.

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