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Inhibition performance of Tobramycin on the dissolution of stainless steel 304 and ingress of hydrogen gas in acid medium

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Abstract

The inhibition performance of Tobramycin (TBN) on stainless steel 304 dissolution and ingress of hydrogen gas in 2N H_3PO_4 and 2N HCl has been analyzed employing mass loss, gasometric and electrochemical studies. The antibiotic seems to be more effective in reducing the dissolution of steel in 2N H_3PO_4 than in 2N HCl. Potential-Current plots evidently pointed out that the inhibitor follows mixed mode of inhibition in acidic media. Hydrogen permeation and EIS measurements have confirmed that TBN retards the corrosion of SS 304 effectively in both the acids . The theoretical values of E_{HOMO}, E_{LUMO}, ΔE and dipole moment in the presence of inhibitor confirmed its effective adsorption on SS 304 surface.

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

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1.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 careful analysis of literature studies clearly reveal that no systematic approach is existing on the inhibitive action of Tobramycin (TBN) in high aggeresive acid solutions.. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair of electrons on nitrogen amino groups of CMZ and delocalization of electrons of pyran-diol moiety of the present drug ease the adsorption of the compound on surface of SS 304 . All the above investigations depict a general information that no significant data is seen on the performance of tobramycin as effective corrosion inhibitor and in bringing down the ingress of hydrogen gas through steel during pickling . It falls under the class of amino glycoside antibiotic resulting from Streptomyces tenebrarius and used to heal a variety of bacterial infections, mostly Gram-negative diseases.

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2.Experimental

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 employed for mass 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 used for potential-current plots and EIS measurements.

The compound was mainly monitored by a mass loss studies as reported by Madhavan et al [9]. Both cathodic and anodic potential- current curves were recorded 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 performed using standard procedure of Devanathan and Stachurski's two compartment cell, as described earlier.[9] Double layer capacitance (Cdl) and charge transfer resistance values (R,) were obtained using EIS measurements .

3. RESULTS AND DISCUSSION

3.1 Mass loss and Gasometric measurements

Table 1 shows the values of inhibition efficiency for various concentrations of tobramycin for the corrosion of SS 304 in 2N HCl and 2N H_3PO_4 obtained from mass loss and gasometric measurements. It is noticed that the inhibitor retards the dissolution of stainless steel in both acids, but more effectively in H_3PO_4 . This can be ascribed to the slighter adsorption of sulphate ions on the steel surface, thereby allowing more space for the tobramycin compound to get adsorbed. But in the case of HCl , the stronger adsorption of the chloride ions on the metal surface favour less space for adsorption of inhibitor. So in H_3PO_4 ,the coverage of the SS 304 by the inhibitor is considerably greater , giving rise to higher values of inhibition performance for all concentrations of the antibiotic used. The structure of the compound is given in Figure 1.

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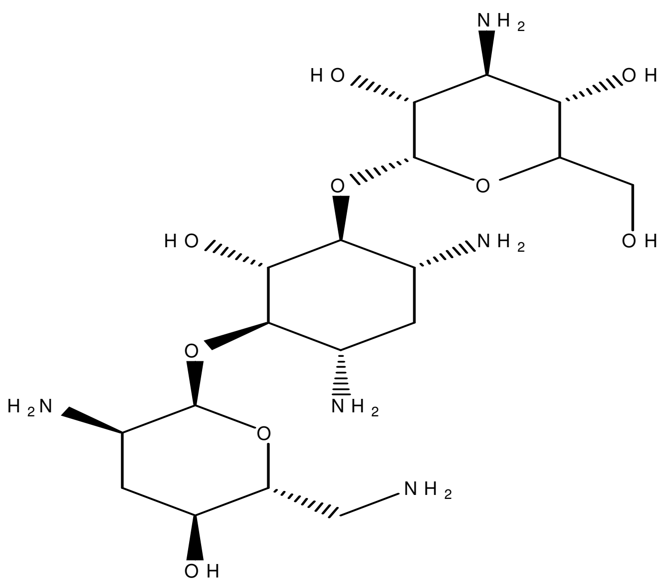


Figure 1.Structure of Tobramycin

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 the amino groups and the positively charged metal surface [10].

2.The interactions between delocalized electrons of the pyran-diol moieties and the positively charged metal surface [11].

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

3.2 Potential-Current plots

Table 2(a) and 2(b) gave the results of potential-current plots such as Tafel slopes (b_a and b_c),corrosion current (I_{corr}) and corrosion potential (E_{corr}) and inhibition efficiency obtained from potentiodynamic polarization studies for SS 304 in 2N HCl and 2N H_3PO_4 containing various concentrations of antibiotic molecule. It can be visualized from this table that results of Tafel slopes and I_{corr} are very much similar to those reported earlier [12,13.] Further it is established that increasing concentrations of tobramycin increases the values of both b_a and b_c in random way justifying that the inhibition of corrosion of SS 304 in both the acids falls under mixed control. Values of E_{corr} is moved to positive direction in the presence of different concentrations of inhibitor. This can be attributed to the formation of strongly adsorbed inhibitor layer on the metal surface. The presence of increasing dosage of inhibitor molecule significantly retards I_{corr} values in both the acids. It can also be noticed that most of the values of inhibition efficiency obtained by mass loss and potential-curve studies agree very well.

3.3 Hydrogen permeation measurements

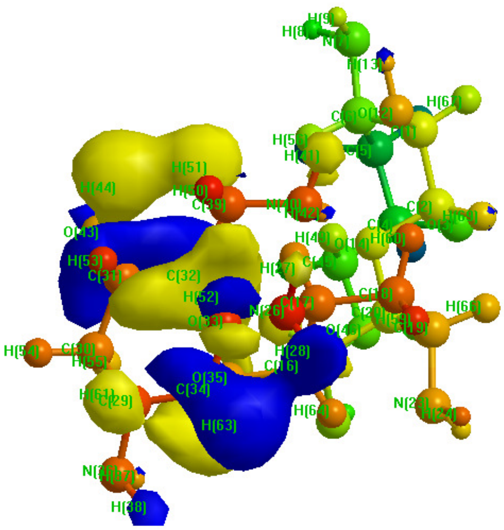
The results of hydrogen permeation measurements for the dissolution of stainless steel 304 in the presence and absence of the tobramycin are given in Table 3.Hydrogen permeation currents for mild steel in 2N HCl is more, because of the highly reactive nature of chloride ions. It can be obtained from the table that the existence of inhibitor in both acids bring down the permeation current and does not favour the ingress of hydrogen gas into SS 304 . The declining trend in permeation currents can be accredited to the effective formation of protective layer formed on the surface of metal surface [14,15] . It can be seen from the table that the decrement of permeation current is more, if the concentration of Clotrimazole is more.

3.4 Impedance studies

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 found in table that the values of R_t is seen to increase with enhancement of TBN concentrations in both the acids. Values of double layer capacitance are confirming that steel dissolution is more in 2N HCl than 2N H_3PO_4 .It is noticed that values of C_{dl} are lowered by increasing concentrations of TBN in acidic media. This can be attributed to the effective adsorption of the antibiotic molecule on the surface of SS 304 with increase in its dosage to the electrolyte.

A plot of surface coverage (ø) versus log C gave a straight line demonstrating that the adsorption of TBN on SS 304 surface from both acids obeys Temkin's adsorption isotherm [16]. This is chief support to corrosion inhibition by this molecule , as a result of its adsorption on the surface of SS 304.

3.5 Quantum chemical studies:



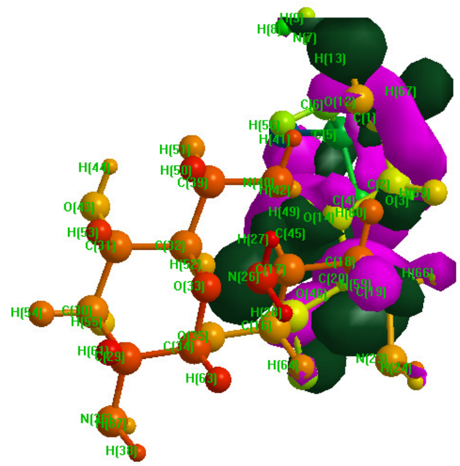


Fig. 2. Highly Occupied MO's of TBN

Fig.3.Lowest unoccupied MO's of TBN

The computed quantum chemical 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 summarized in Table 2. From figure 2 and 3 , it can be observed that HOMO and LUMO energy orbital's were strongly distributed on amino groups and and pyran-diol for HOMO and LUMO structures establishing that the tobramycin posses good adsorption centers [17-19] and this is in agreement with publications of molecular orbital studies confronting that π electrons and N atoms are liable for inhibition activity[20].

According to Hari Kumar et al [21], when a molecule has similar distribution of electronic orbital's, its inhibition performance could be associated with the energy values of HOMO and LUMO and the difference in values between them. It has been extensively 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. Also, lower E_{LUMO} values , favour 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 measured as an vital data . Smaller the value of ΔE of an inhibitor, greater is the inhibition efficiency of that compound . It is further claimed that, large values of dipole moment will considerably raise the adsorption of the compound on metal surface [22-24].

4. Conclusions

1. Tobramycin retards the dissolution of the corrosion of SS 304 in both acids, but shows a better performance in 1N $H3PO_4$.

2. The inhibition of corrosion of stainless steel by the compound in both the acids H_3PO_4 falls under mixed control.

3. The presence of inhibitor molecule in both the acids is found to reduce the extent of hydrogen permeation current through SS 304 surface.

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4. R_t and C_{dl} values studied from impedance measurements prove the impressive performance of the inhibitor.

5. The adsorption of the compound on SS 304 surface follows Temkin's adsorption isotherm.

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

Concentration of Inhibitor (mM)	Inhibition efficiency (%)			
	HCl		H_3PO_4	
	Weight loss Studies	Gasometric measurements	Weight loss studies	Gasometric measurements
5	57	56.8	70	70.8
10	61	60.5	77	77.6
15	67	67.2	85	85.3
20	75	75.0	89	88.7

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

Concentration of Inhibitor (mM)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} $\mu A\ cm^{-2}$	Inhibition efficiency (%)
		b_a	b_c		
Blank	−513	68	123	549	---
5	−489	75	122	274	50.9
10	−483	63	132	208	62.1
15	−475	71	128	197	64
20	−465	96	146	125	77.2

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Table 2.b Corrosion kinetic parameters of SS 304 in 2N H_2SO_4 in the presence of different concentrations of tobramycin obtained from galavanostatic 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	-919	76	134	269	---
5	-886	73	143	80.4	70.2
10	-875	75	138	59.7	77.6
15	-866	62	146	39.8	85
20	-860	51	138	30.2	89

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Table 3. Values of permeation current for the corrosion of mild steel in 2N HCl and 2N H_3PO_4 in the presence of different concentrations of Clotrimazole.

Concentration of Inhibitor (mM)	Steady state permeation current (μA)	
	1M HCl	1M H_3PO_4
Blank	23.6	19.5
5	21.0	17.5
10	20.1	12.6
15	16.5	10.8
20	13.3	6.4

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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)	HCl		H_3PO_4	
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}
Blank	5.32	237	6.97	184.4
5	34	167	38	165
10	42.2	127	54	122
15	70.1	115	62	100.2
20	91.9	101.2	130	68.2

Table 5: Quantum chemical parameters for Clotrimazole

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Tobramycin	21.86	20.26	8.95	5.4

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