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Corrosion and hydrogen permeation investigations of Stainless steel 304 in acidic solutions

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Abstract

The influence of **Clotrimazole** (CMZ) on corrosion and hydrogen permeation through Stainless steel 304 in 2N H_3PO_4 and 2N HCl has been studied using weight loss measurements and various electrochemical techniques. The inhibitor is found to be more effective in retarding the metal corrosion in H_3PO_4 than in HCl. Potentiodynamic polarization studies clearly indicate that CMZ behaves as a mixed inhibitor. Hydrogen permeation studies and AC impedance measurements also proved an excellent performance of the compound in H_3PO_4. The adsorption of this compound on the mild steel surface obeys Temkin's adsorption isotherm which is further validated by Quantum chemical calculations.

Keywords: Corrosion inhibitor, Clotrimazole, hydrogen permeation

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1. Introduction

Antibiotics and allied drugs have been reported in recent years as corrosion inhibitors because of their less toxicity [1-3]. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. While extensive investigations have been carried out on inhibitor properties of antifungal drugs , due attention has

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not yet been paid to a systematic study on Clotrimazole as potential corrosion inhibitors for stainless steel alloys in high aggressive acidic media, i.e. 2N HCl and 2N H_3PO_4 . However, very few reports are available using clotrimazole as corrosion inhibitors for aluminium in HCl medium [4]. Most of the effective organic inhibitors have hetero atoms such as O, N, S containing multiple bonds in their molecules through which they can adsorb on the metal surface [5-8]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair of electrons on nitrogen imidazole ring of CMZ and delocalization of π electrons of three benzene rings of the present drug establishes the adsorption of the compound on SS 304 surface. All the above studies expose one common observation that Clotrimazole can be regarded as excellent corrosion inhibitors. But studies on the influence of Clotrimazole on hydrogen permeation through steel substrate during pickling are very scarce. It belongs to the class of imidazole and triazole derivatives for topical use and utilized in the treatment of fungal infection. A good inhibitor should have the following two important requisites: (1) it should have very good inhibition efficiency and (2) it should bring down the hydrogen permeation current to a considerable extent. Some organic compounds offer very high values of inhibition efficiency, but they have a insignificant effect in plummeting the hydrogen permeation current and vice versa. Compounds which come under this class produce hydrogen embrittlement in a later stage by the combination of permeated atomic hydrogen. This delayed failure creates cracking, pitting, breakage, etc., on the metal surface.

2. Experimental

Stainless steel 304 specimens of compositions, C= 0.08%, Si = O%, Ni = 8%, Cr = 18% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight loss and hydrogen permeation studies. A mild steel cylindrical

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rod of the same composition as above and embedded in araldite resin with an exposed area of 0.283 cm^2 was used for potentiodynamic polarization and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier. [9] Both cathodic and anodic polarisation curves were recorded potentiodynamically (1 mA s^{-1}) using corrosion measurement system BAS Model: 1OOA computerised electrochemical analyzer (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). Platinum foils, Hg/Hg2Cl2/KCl (satd) were used as auxiliary and reference electrodes, respectively. The hydrogen permeation study was carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell, as described earlier.[4] Double layer capacitance (Cdl) and charge transfer resistance values (R,) were obtained using AC impedance measurements as described in an earlier publication." The surfaces of corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200- 700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan).

3. RESULTS AND DISCUSSION

3.1 Weight loss and Gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of Clotrimazole for the corrosion of mild steel in 2N HCl and 2N H_3PO_4 obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of mild steel in both acids, but more effectively in H_3PO_4. This can be attributed to the lesser adsorption of sulphate ions on the metal surface, thereby leaving more space for the organic molecules to get adsorbed. But in HCl the stronger adsorption of the chloride ions on the metal surface leaves less space for organic molecules to get adsorbed. So in H_3PO_4, the coverage of the metal surface by the organic molecules is significantly more, giving rise to higher values of inhibition efficiency for all concentrations of the compound used [9].

The structure of the compound is given in Figure 1.

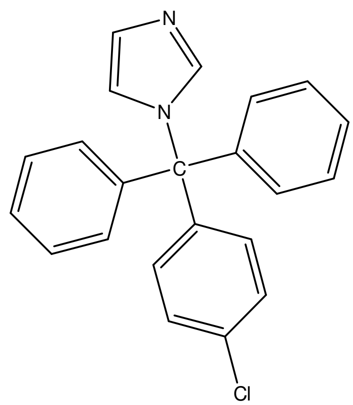

Figure1. Structure of Clotrimazole.

The inhibition of corrosion of brought about by Clotrimazole can be due to the following interactions:

1. The interaction between the lone pairs of electrons of the nitrogen atoms of the imidazole ring and the positively charged metal surface [10].
2. The interactions between delocalized electrons of the benzene groups and the positively charged metal surface [11].

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

3.2 Potentiodynamic polarization studies

Table 2(a) and 2(b) give values of corrosion kinetic parameters 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 curves for mild steel in 2NHCl and 2N H_3PO_4 containing different concentrations of inhibitor. It can be seen from this table that values of Tafel slopes and I_{corr} are very much similar to those reported earlier [12-13]. Further it is ascertained that increasing concentrations of Clotrimazole enhances the values of both b_a and b_c in irregular fashion confirming that the inhibition of corrosion of SS 304 in both acids is under mixed control. Values of E_{corr} are shifted to less negative values in the presence of different concentrations of CMZ. This can be ascribed to the formation of closely adherent adsorbed film on the metal surface. The presence of increasing concentrations of Clotrimazole retards I_{corr} values in both the acids. It can also be seen that most of the values of inhibition efficiency obtained by weight loss measurements and potentiodynamic polarization studies agree very well.

3.3 Hydrogen permeation measurements

Hydrogen permeation measurements results for the corrosion of mild steel in the presence and absence of the inhibitor are presented in Table 3.Hydrogen permeation current for mild steel in 2N HCl is more, because of the aggressive nature of chloride ions. It can be seen from the table that the presence of Clotrimazole in both acids decreases the permeation current and does not favor the ingress of hydrogen gas into SS 304. The reduction in permeation current can be attributed to the strong adsorption of the compound on the mild steel surface [12-15].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}) derived from Nyquist plots are shown in table 4.It can be found in table that the values of R_t is seen to increase with enhancement of CMZ concentrations in both the acids. Values of double layer capacitance are establishing that steel dissolution is more in 2N HCl than 2N H_3PO_4 .It is found that values of C_{dl} are lowered by increasing concentrations of antibiotic in both the acids. This can be ascribed to increased adsorption of the CMZ molecule on the metal surface with increase in its concentration.

A plot of surface coverage (ø) versus log C presents a straight line illustrating that the adsorption of CMZ on SS 304 surface from both acids follows Temkin's adsorption isotherm. This is major evidence to corrosion inhibition by this compound, as a consequence of its adsorption on the metal surface.

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3.5 Quantum chemical studies:

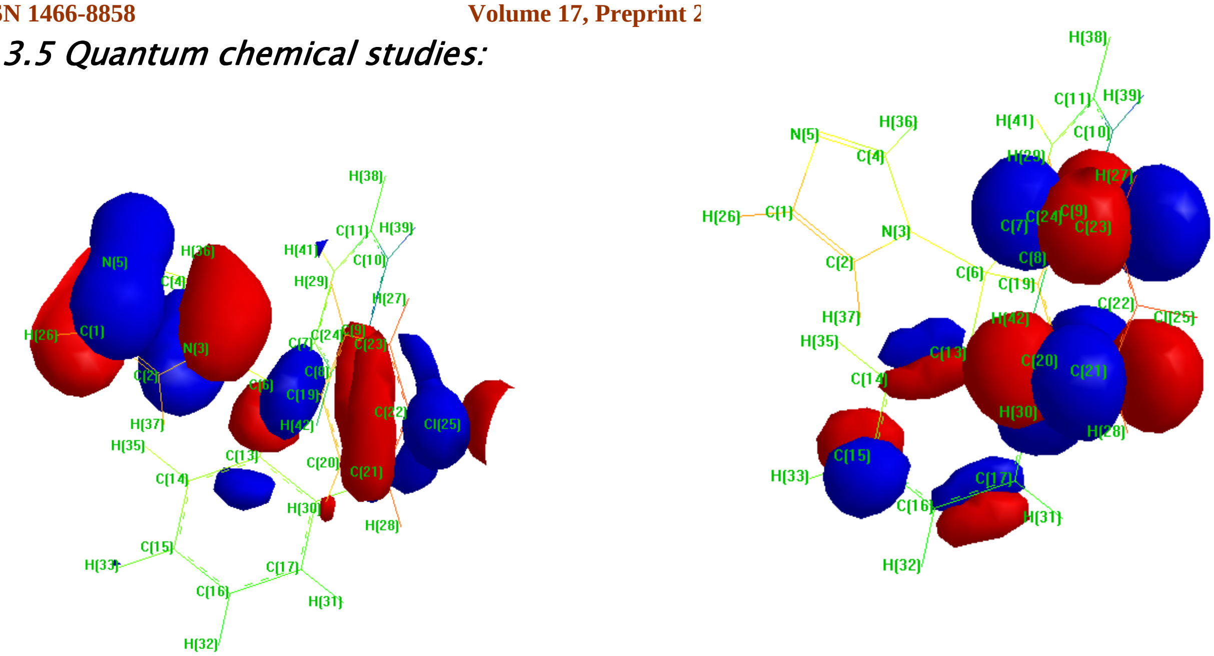

Fig 2.(a) Highly Occupied MO's of inhibitors Fig.2(b)LUMO's of inhibitors

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 4, it can be observed that HOMO and LUMO energy orbital's were strongly distributed on benzene groups and imidazole moiety for HOMO structure nitrogen and almost nil, on pyridine group in the case of LUMO establishing that the benzene moiety contains effective adsorption centres [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 karthikeyan et al. [21], when a molecule possesses similar frontier orbitals, its inhibition effectiveness can be allied to the energy levels of HOMO and LUMO and the distinction between them. It has been significantly claimed that, higher the value of E_{HOMO}, larger is the ease for an inhibitor to release electrons to unfilled d orbital of metal atom and higher is the inhibition performance. Also, lower E_{LUMO} values, felicitate acceptance of electrons from metal atom to form feedback bonds. Hence the gap between HOMO–LUMO energy levels of molecules was considered as an important parameter. Smaller the value of ΔE of an inhibitor, greater is the inhibition efficiency of that compound. It has been reported that, large values of dipole moment will appreciably increase the corrosion inhibition [22-24].

4. Conclusions

1. **Clotrimazole** inhibits the corrosion of SS 304 in both acids, but shows a better performance in 1N H3PO4.
2. The inhibition of corrosion of stainless steel in 2N HCl than 2N H_3PO_4, by the inhibitor is under mixed control.
3. The presence of inhibitor molecule in both the acids is found to reduce the extent of entry of hydrogen through steel surface.
4. R_t and C_{dl} values studied from impedance measurements prove the improved performance of the compound.
5. The adsorption of the inhibitor 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 H3PO4 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
2	79	794	85.2	85.8
4	83.2	83.5	94.1	94.6
12	91.0	91.2	95.4	95.5
36	94.4	94.7	98.2	98.7

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Table 2.a Corrosion kinetic parameters of SS 304 in 2N HCl in the presence of different concentrations of Clotrimazole 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	-510	67	122	2.89	---
2	-487	74	120	0.53	79
4	-481	68	135	0.40	82.2
16	-472	72	129	0.26	91.2
32	-464	94	144	0.11	93.7

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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 Clotrimazole 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	77	133	2.45	---
2	-884	72	141	0.29	85.0
4	-873	76	137	0.12	94.2
16	-866	59	145	0.06	94.7
32	-861	50	136	0.02	98.5

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	22.7	19.7
2	21.3	17.8
4	20.3	13.5
16	17.1	11.3
32	14.2	7.9

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	5.3	235	6.9	185
2	32	168	34	167
4	40.3	131	48	125
16	73.1	118	82	108.3
32	92.0	101	127	78.4

Table 5: Quantum chemical parameters for Clotrimazole

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Clotrimazole	-1.891	-10.841	8.95	5.4