

# Hydrogen permeation studies on the corrosion of stainless steel in acid medium using an eco-friendly inhibitor

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## Abstract

The analysis of hydrogen gas ingress during the corrosion of stainless steel in pickling acid such as 2N H<sub>2</sub>SO<sub>4</sub> in the presence and absence of an ecofriendly inhibitor Thiamphenicol[TPC] has been carried out using mass loss, gasometric and electrochemical studies. The antibiotic seems to be more effective in plummeting the dissolution of steel in 2N H<sub>2</sub>SO<sub>4</sub>. Potentiodynamic polarization clearly indicated that the inhibitor follows mixed mode of inhibition in 2N H<sub>2</sub>SO<sub>4</sub> medium. Hydrogen permeation and EIS measurements have confirmed that the present antibiotic checks the dissolution of SS 304 efficiently in sulphuric acid. The theoretical values of E<sub>HOMO</sub>, E<sub>LUMO</sub>, ΔE and dipole moment in the presence of inhibitor established its effective adsorption on SS 304 metal surface.

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

## 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 Thiamphenicol [TPC] in high aggressive acid solutions.. The corrosion inhibiting property of this antibiotics is attributed to its molecular structure. The unshared pair of electrons on nitrogen of ethyl acetamido groups of TPC molecules and delocalization of electrons of methyl sulphonyl moiety of the present drug ease the adsorption of the compound on surface of stainless steel. All the

above investigations depict a general information that no significant data is seen on the performance of this eco friendly molecules as effective corrosion inhibitor and in bringing down the ingress of hydrogen gas through steel during pickling . It falls under the class of methyl sulphonyl acetamido antibiotic and used to heal a variety of bacterial infections.

## 2.Experimental

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

C= 0.08% , Si = 0%, Ni = 8%, Cr = 18% and Fe= balance with exposed area of  $4 \times 1 \times 0.020$  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  $0.3 \text{ cm}^2$  was used for potential–current plots and EIS measurements.

The compound was mainly monitored by a Mass loss studies as investigated by Madhavan et al [9]. Both cathodic and anodic potential– current curves were recorded potentiodynamically ( $1 \text{ mV s}^{-1}$ ) using corrosion measurement system BAS Model: 100A computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil of  $4 \text{ cm}^2$ ,  $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}_{(\text{satd})}$  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 ( $R_c$ ) were obtained using EIS measurements .

## 3. RESULTS AND DISCUSSION

### *3.1 Mass loss and Gasometric measurements*

Table 1 showed the values of inhibition efficiency for various concentrations of Eco friendly inhibitor for the corrosion of SS 304 in  $2\text{N H}_2\text{SO}_4$  obtained from weight loss and gasometric measurements. It was noticed that the inhibitor brings down the corrosion of stainless steel effectively in  $\text{H}_2\text{SO}_4$  . This can be accredited to the lesser

adsorption of sulphate ions on the steel surface, thereby allowing more space for this eco-friendly inhibitor to get adsorbed on SS 304 in 2N  $\text{H}_2\text{SO}_4$ . Hence in sulphuric acid medium, the coverage of the SS 304 by the TPC molecules is noticeably greater, giving rise to higher values of inhibition performance for all concentrations of the antibiotic used. The electronic structure of the compound is given in Figure 1.

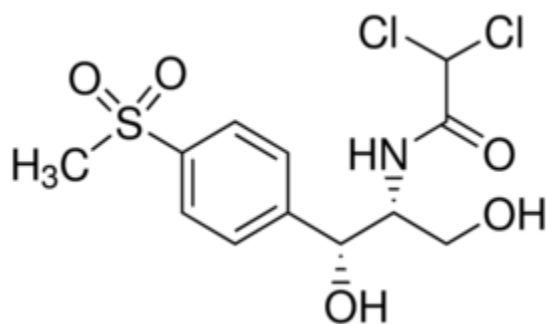


Figure 1. Structure of Thiamphenicol

The retardation on the dissolution of SS 304 in acid medium favored by TPC molecules were involving the following interactions:

1. The interaction between the lone pairs of electrons of the nitrogen atoms of the ethyl acetamido groups of inhibitor and the positively charged metal surface [10].
2. The interactions between delocalized electrons of the methyl sulphonyl groups and the positively charged metal surface of the green inhibitor [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 Potentiodynamic polarization measurements***

Table 2(a) and 2(b) gave the results of potential-current plots such as Tafel slopes ( $b_a$  and  $b_c$ ), corrosion current ( $I_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) and inhibition efficiency obtained from potentiodynamic polarization studies for SS 304 in 2N  $\text{H}_2\text{SO}_4$  containing various concentrations of antibiotic molecule. It can be envisaged from table that results of Tafel slopes and  $I_{\text{corr}}$  are very much similar to those reported earlier [12,13.] Further it is well-known that increasing concentrations of TPC

inhibitor increases the values of both  $b_a$  and  $b_c$  in unequal fashion justifying that the inhibition of corrosion of SS 304 in 2N  $H_2SO_4$  follows mixed mode of interaction. Values of  $E_{corr}$  was progressed to positive direction in the presence of different concentrations of TPC molecules. This can be ascribed to the formation of firmly adsorbed inhibitor film on the SS 304 metal surface. The presence of increasing quantity of inhibitor molecule significantly retards  $I_{corr}$  values in 2N  $H_2SO_4$ . It can also be observed that most of the values of inhibition efficiency obtained by mass loss and potentiodynamic polarization studies agree very well.

### ***3.3 Hydrogen permeation studies***

The results of ingress of hydrogen gas studies for the dissolution of stainless steel 304 in the presence and absence of the TPC inhibitor are given in Table 3. It can be concluded from the table that the existence of inhibitor in 2N  $H_2SO_4$  bring down the permeation current and does not encourage the ingress of hydrogen gas into SS 304. The declining trend in permeation currents can be attributed to the active formation of protective layer on the surface of metal surface [14,15]. It can be realized from the table that the decrement of permeation current is more, if the concentration of Thiamphenicol inhibitor is high.

### ***3.4 Impedance analysis***

Values of charge transfer resistance ( $R_t$ ) and double layer capacitance ( $C_{dl}$ ) obtained from EIS measurements are presented in table 4. It can be found in table that the values of  $R_t$  is seen to escalation with enrichment of green compound dosages in 2N  $H_2SO_4$ . Values of double layer capacitance are confirming that steel dissolution is more in 2N  $H_2SO_4$  in the absence of Thiamphenicol. It was observed that values of  $C_{dl}$  are lowered by increasing concentrations of inhibitor in sulphuric acid medium. This can be attributed to the effective adsorption of the antibiotic molecule on the surface of SS 304 with increase in its quantity to the electrolyte.

A plot of surface coverage ( $\theta$ ) versus  $\log C$  gave a straight line signifying that the adsorption of green inhibitor on SS 304 surface from 2N  $H_2SO_4$  follows Temkin's adsorption isotherm [16]. This is main sustenance to corrosion inhibition by this molecule, as a result of its adsorption on the surface of SS 304.

#### **4. Conclusions**

1. TPC, an eco friendly inhibitor retards the the corrosion of SS 304 in 2N H<sub>2</sub>SO<sub>4</sub> effectively.
2. The inhibition of corrosion of stainless steel by the compound in pickling medium falls under mixed control.
3. The presence of Thiamphenicol molecule in 2N H<sub>2</sub>SO<sub>4</sub> found to reduce the ingress of hydrogen gas through SS 304 surface.
4. R<sub>t</sub> and C<sub>dl</sub> values studied from impedance measurements prove the impressive performance of the inhibitor.
5. The adsorption of the compound on SS 304 surface obeyed Temkin's adsorption isotherm.

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**Table 1. Values of inhibition efficiency for the corrosion of mild steel in 2N H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of Eco friendly inhibitor obtained from weight loss and gasometric measurements.**

Concentration of Inhibitor (mM)	Inhibition efficiency	
	Weight loss Studies	Gasometric measurements
10	67	66.7
20	89	89
30	97	96.7
40	85	84.8

Table 2. Corrosion kinetic parameters of SS 304 in 2N H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of Eco friendly inhibitor obtained from potentiodynamic polarization studies.

Concentration of Inhibitor (mM)	E <sub>corr</sub> (mV)	Tafel slopes in mV in dec <sup>-1</sup>		I <sub>corr</sub> mA cm <sup>-1</sup>	Inhibition efficiency (%)
		b <sub>a</sub>	b <sub>c</sub>		
No Inhibitor ---	-376	75	131	180	
10 81.8	-372	73	138	48.7	
20 86.7	-361	61	140	35.6	
30 97.4	-358	50	139	6.96	



**Table 3. Values of permeation current for the corrosion of mild steel in 2N H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of inhibitor.**

Concentration of Inhibitor (mM)	Permeation current (μ.A)
	Pickling acid
No inhibitor	19.9
10	12.3
20	10.2
30	6.5

**Table 4. Impedance parameters for the corrosion of Stainless steel 304 in 2N H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of green compound**

Concentration of Inhibitor (mM)	H <sub>2</sub> SO <sub>4</sub>	
	Charge Transfer resistance (R <sub>t</sub> ) Ohm.cm <sup>2</sup>	Double layer capacitance (C <sub>dl</sub> ) μF.cm <sup>-2</sup>
No inhibitor	6.97	185

10	54	35.15
20	62	24.79
30	130	4.63