Studies on the Controlled Dissolution of Stainless Steel 304 in Acidic Medium

K.Mohanam*, A.Sankar Kumar, T.Mari

[1]School of Mechanical Engineering, VIT University, Vellore -632014 , India

Abstract : The inhibition performance of an antibiotic namely Claulenic acid (CLA) on stainless steel 304 dissolution in 2N HCl has been analyzed using theoretical values of E_{HOMO}, E_{LUMO}, ΔE and dipole moment mass loss, gasometric   and electrochemical studies. The antibiotic   seems to be more effective in reducing the dissolution of steel   in 2N HCl. Galvanostatic polarization curves clearly showed out that the inhibitor follows   mixed mode of inhibition in acidic media. The adsorption of inhibitor on SS 304 surface followed Temkin's adsorption isotherm.

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 exocyclic 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 Claulenic Acid (CLA) in high aggressive 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 CLA 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 Claulenic acid 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.

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 studies. 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]. cathodic and anodic potential- current curves were recorded galvano statically (1 mA 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. Double layer capacitance (Cdl) and charge transfer resistance values (R,) were obtained using EIS measurements. A special

computational program has been used to interpret theoretical values of E_{HOMO}, E_{LUMO}, ΔE and dipole moment of CLA in 2N HCl.

3. Results and Discussion

3.1 Mass loss and Gasometric measurements

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

Concentration of Inhibitor (mM)	Inhibition Efficiency	
	Weight loss Studies	Gasometric measurements
3	57	57.4
30	68	68.6
150	89	88.5
200	97	96.5

Table 1 shows the values of inhibition efficiency for various concentrations of Claulenic acid for the corrosion of SS 304 in 2N HCl obtained from mass loss and gasometric measurements. It is noticed that the inhibitor reduces the corrosion of stainless steel in in 2N HCl. Also, 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.
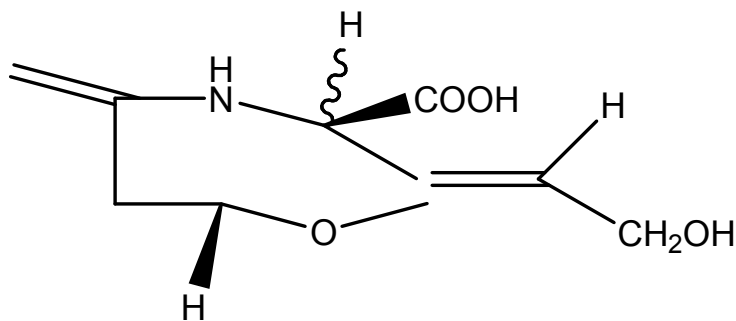
Figure 1.Structure of Claulenic acid

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

1. The interaction between the lone pairs of electrons of the nitrogen atoms of the acetyl amino groups of hydroxyl ethylidiece moiety of CLA and the positively charged metal surface [10].
2. The interactions between delocalized electrons of the aza oxo bicyclo 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 Potential-Current plots

Table 2. Corrosion kinetic parameters of SS 304 in 2N HCl in the presence of different concentrations of Claulenic acid obtained from galvanostaic 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	-510	66.5	124	535	---
3	-484	72.2	122	232.7	56.5
30	-475	63.2	131	170.13	68.2
150	-470	70.4	120.3	60.4	88.7
200	-464	67.8	145.2	18.73	96.5

Table 3.Impedance parameters for the corrosion of Stainless steel 304 in 2N HCl in the presence of different concentrations of Claulenic acid.

Concentration of Inhibitor (mM)	HCl	
	Charge Transfer resistance (R_t) $Ohm.cm^2$	Double layer capacitance (C_{dl}) $\mu F.cm^{-2}$
Blank	5.32	287
3	66	78.2
30	82.5	54.8
150	100.2	26.5
200	160.4	3.24

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 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 Claulenic acid increases the values of b_a and b_c in random way justifying that the inhibition of corrosion of SS 304 in acid medium 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 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 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 CLA concentrations in the acids. Values of double layer capacitance are confirming that steel

dissolution is more in 2N HCl. It is noticed that values of C_{dl} are lowered by increasing concentrations of CLA 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.

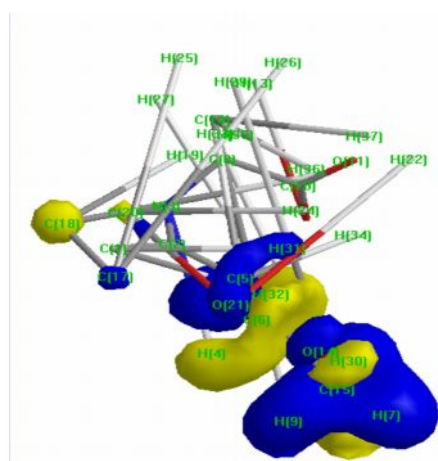**Table 4: Quantum chemical parameters for Claulenic acid**

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
CLA	23.799	22.57	1.229	5.563

A plot of surface coverage (ø) versus log C gave a straight line demonstrating that the adsorption of CLA on SS 304 surface from 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.

3.4 Quantum chemical studies:
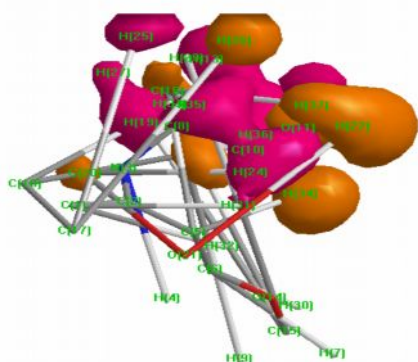
Fig. 2. Highly Occupied MO's of CLA   Fig.3.Lowest unoccupied MO's of CLA

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 nitrogen groups and and hydroxyl ethylidine moiety for HOMO and LUMO structures establishing that the Claulenic acid 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. Claulenic acid retards the dissolution of the corrosion of SS 304 in 2N HCl.
2. The inhibition of corrosion of stainless steel by the compound falls under mixed control.
3. The presence of inhibitor molecule in 2N HCl acid medium is found to reduce the extent of hydrogen permeation current through SS 304 surface.
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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