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Hydrogen permeation analysis of corrosion of stainless steel in pickling solution

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Abstract: The hydrogen permeation analysis during the corrosion of stainless in pickling acid such as 2N H3PO4 in the presence and absence of an ecofriendly inhibitor 6R,7R)-7-{[(2R)-2-amino-2-(1-cyclohexa-1,4-dienyl)acetyl]amino}-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid has been cariedout 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 Potentiodynamic polarization clearly indicated that the inhibitor follows mixed mode of inhibition in 2N H_3PO_4. Hydrogen permeation and EIS measurements have confirmed that the present antibiotic retards the corrosion of SS 304 effectively in pickling acid. 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.

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 6R,7R)-7-{[(2R)-2-amino-2-(1-cyclohexa-1,4-dienyl)acetyl]amino}-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid in high aggeresive acid solutions. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The unshared pair of electrons on nitrogen amino groups of inhibitor 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 Eco friendly inhibitor 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 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 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 weight loss studies as investigated 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 Weight loss and Gasometric measurements

Table 1. Values of inhibition efficiency for the corrosion of mild steel in 2N H_3PO_4 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
2	55	56.2
20	63	62.6
50	85	84.6
100	94	93.5

Table 1 shows the values of inhibition efficiency for various concentrations of Eco friendly inhibitor for the corrosion of SS 304 in 2N H_3PO_4 obtained from weight loss and gasometric measurements. It is noticed that the inhibitor brings down the corrosion of stainless steel effectively in H_3PO_4 . This can be attributed to the lesser adsorption of phosphate ions on the steel surface, thereby allowing more space for the Eco friendly inhibitor to get adsorbed on SS 304 in 2N H_3PO_4 . 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 space filling electronic structure of the compound is given in Figure 1.

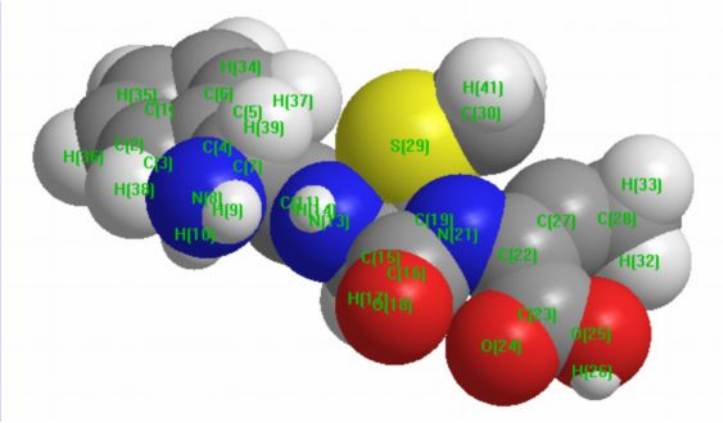

Figure 1. Space filling electronic Structure of 6R,7R)-7-{[(2R)-2-amino-2-(1-cyclohexa-1,4-dienyl)acetyl]amino}-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid

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

1. The interaction between the lone pairs of electrons of the nitrogen atoms of the acetyl amino groups of cyclohexa dienyl moiety of inhibitor and the positively charged metal surface [10].

2. The interactions between delocalized electrons of the oxo thia 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 Potentiodynamic polarization measurements

Table 2. Corrosion kinetic parameters of SS 304 in 2N H_3PO_4 in the presence of different concentrations of Eco friendly inhibitor 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		
No Inhibitor	-918	75	131	268	---
2	-885	72	142	65.9	75.4
20	-872	73	138	48.7	81.8
50	-861	61	140	35.6	86.7
100	-858	50	139	6.96	97.4

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 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 Eco friendly inhibitor increases the values of both b_a and b_c in irregular fashion extenuating that the inhibition of corrosion of SS 304 in 2N H_3PO_4 follows mixed type. Values of E_{corr} is moved to positive direction in the presence of different concentrations of inhibitor. This can be accredited to the formation of sturdily adsorbed inhibitor film on the metal surface. The presence of increasing quantity of inhibitor molecule ominously retards

I_{corr} values in 2N H_3PO_4 . It can also be noticed that most of the values of inhibition efficiency obtained by weight loss and potentiodynamic polarization studies agree very well.

3.3 Hydrogen permeation measurements

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

Concentration of Inhibitor (mM)	Permeation current (µ.A)
	Pickling acid
No inhibitor	19.9
2	17.3
20	12.3
50	10.2
100	6.5

The results of hydrogen permeation measurements for the dissolution of stainless steel 304 in the presence and absence of the Eco friendly inhibitor are given in Table 3. It can be inferred from the table that the existence of inhibitor in 2N H_3PO_4 bring down the permeation current and does not encourage the permeation 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 Eco friendly inhibitor 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 green compound concentrations in 2N H_3PO_4. Values of double layer capacitance are confirming that steel dissolution is more in 2N H_3PO_4 . It is noticed that values of C_{dl} are lowered by increasing concentrations of inhibitor in pickling 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.

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 green compound

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}
No inhibitor	5.32	237	6.97	185
2	34	107.5	38	45.51
20	42.2	86.5	54	35.15
50	70.1	36.26	62	24.79
100	91.9	16.59	130	4.63

A plot of surface coverage (ø) versus log C gave a straight line signifying that the adsorption of green inhibitor on SS 304 surface from 2N H_3PO_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. Eco friendly inhibitor retards the the corrosion of SS 304 in 2N H3PO4 effectively.
2. The inhibition of corrosion of stainless steel by the compound in pickling medium falls under mixed control.
3. The presence of inhibitor molecule in 2N H_3PO_4 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 obeys Temkin's adsorption isotherm.

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