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Reduction of hydrogen embrittlement and green inhibition of stainless steel pipes in acid environment

K.Raja, P.A.Jeeva , S.Karthikeyan*

Manufacturing Division, SMBS, VIT University, Vellore – 632014, India.

Abstract: The dissolution behavior of SS 304 pipes in 2M Sulphuric acid with green inhibitor (namely neomycin) as corrosion inhibitor has been studied by Mass loss, Potentiodynamic polarization, electrochemical impedance spectroscopy and hydrogen permeation studies. All these techniques confirm that the green inhibitor retards the dissolution of steel in sulphuric acid medium.Polarization studies indicated that inhibitors are acted as mixed type. The adsorption of the compounds on SS 304 surface obeys Langmuir adsorption isotherm.

Keywords : antibiotics, hydrogen permeation, corrosion inhibitors, green inhibition.

Introduction

SS 304 is an important category of metals due to its excellent density and conductivity. It is extensively used under different conditions in sheet metal parts in automobile industries .SS 304 is used in industries as pipelines for petroleum industries, storage tanks, reaction vessel and chemical batteries [1]. Acid solutions are extensively used in many industrial processes. Acids are used for acid cleaning, pickling and descaling owing to their chemical properties [2-5]. In general, the great corrosive nature acids may originate lossof metals. Several methods were used to retard the dissolution of metals in acidic medium, but the use of inhibitors is most commonly used [6-10].

The usage of inhibitors is inexpensiveand real method to reduce electrochemical corrosion. Numerous organic compounds which have π bonds and contains hetero atoms such as sulphur, nitrogen, oxygen and phosphorous which allows the adsorption of compounds on the metal surface were reported as corrosion inhibitors by several investigators [11-16] for dissolution of stainless steel in acid medium Research happenings in recent times are geared towards emerging the cheap, non-toxic drugs as environment responsive corrosion inhibitors [17-24].

The literature review indicates that few antibiotics have been reported as corrosion inhibitors for the corrosion of mild steel and aluminium in acidic and alkaline media [25]. Recently, the use of ampicilin as inhibitor for the corrosion of mild steel in 1 M HCl was reported by Harikumar et al [26]. Nevertheless, no tangible report is available for the corrosion inhibition of SS 304 in 2M sulphuric acid with aid of neomycin as inhibitor and hence the present study.

The inhibition efficacies of the compounds were calculated using mass loss, electrochemical techniques. Infrequently the usage of hydrogen permeation measurements and diffuse reflectance studies for this green inhibitor established the prominent performance of the inhibitors. This compound is big enough and amply planar to block more metal surface area.

Experimental Section

Materials

SS 304 specimens of size 1×4 cm² were used for mass loss and electrochemical studies. The aggressive solution of 2 M H₂SO₄ [AR Grade] is used for all the studies. The antibiotic namely niomycinwas procured from the medicine shop and used as such without further purification. The structure of the antibiotics is given in the fig.1.Electrochemical experiments were cariedout using a three electrode cell assembly with stainless steel samples as working electrode, platinum as counter electrode and saturated calomel [SCE] as the reference electrode.

Mass Loss Studies

Weight loss and hydrogen permeation were performed as described earlier [27]. The concentrations of green compound used for weight loss and electrochemical study were from 10×10^{-4} M to 30×10^{-4} M. Stainless steel specimens of size 1×4 cm² were abraded with different emery papers and degreased with trichloroethylene. The cleaned surfaces were then washed with double distilled water,dried out and retained in the desicator. The mass loss study was carried out at room temperature for three hours in 2 M H₂SO₄. The inhibition efficiency (IE%) was determined by the following equation ,

Inhibition Efficiency (IE%) = $(W_o - W_i / W_o) \times 100$ (1)

Where $W_0 \& W_i$ are the weight loss values in absence and presence of the green compound.

Electrochemical Studies

Potentiodynamic polarization measurements were performed in a conventional three electrode cylindrical glass cell, using CH electrochemical analyzer at a scan rate of 10 mV s⁻¹. Before recording the polarization curves the solution was deaerated for 20 min. and the working electrode was maintained at its corrosion potential for 10 minutes until a steady state was obtained. The stainless steel surface was put in to various concentrations of inhibitors in 100 mL of 2 M H_2SO_4 at room temperature. The inhibition efficiency (IE%) was calculated using the equation,

Inhibition Efficiency (IE%) = $(I_0 - I/I_0) \times 100$ (2)

Where I_0 and I are the corrosion current density without and with the green compound respectively.

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -750 mV to +150mV versus the open circuit potential. The corresponding corrosion current (I_{corr}) was recorded. Tafelplots were created by plotting E versus log *I*. Corrosion Potential (E_{corr}), corrosion current density (I_{corr}) and cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures.

Impedancemeasurements were done in the frequency range from 0.1 to 10000 Hz by means of an amplitude of 20 mV and 10 mV peak to peak with an AC signal at the open-circuit potential. Charge transfer resistance ($R_{\rm ct}$) and double layer capacitance ($C_{\rm dl}$) values were obtained from Nyquist plot [28-30]. The percentage inhibition efficiency was calculated from the equation,

Inhibition Efficiency (IE%) = $(R_{ct} - R'_{ct} / R_{ct}) \times 100$ (3)

Where R'_{ct} and R_{ct} are the corrosion current of SS 304with and without inhibitor respectively.

Hydrogen Permeation Studies

The hydrogen permeation study was carried out using an adaptation of reformed nDevanathan and Stachurski's, two compartment cell as described elsewhere [31] Hydrogen permeation current were obtained in the absence and presence of neomycinused in the current study.

Results And Discussion

Mass Loss Studies

The values of inhibition efficiency (IE%), corrosion rate (*CR*) and surface coverage (θ) calculated for green inhibitor in 2 M H₂SO₄ at different concentrations from the mass loss data is summarized in the Table 1. It is manifested that inhibition efficiency increases with increase in the inhibitor concentration. It was alsoperceived that corrosion rate decreases with increase in green inhibitor concentration. It was noted that inhibitors inhibit the stainless steel corrosion at all the concentrations used in the study. Maximum inhibition efficiency is observed at 30×10^{-4} M concentrations of the inhibitor.

Inhibitor	Weight	Inhibition	Surface	
Conc.	loss	efficiency	coverage	
(M)	(g)	(<i>IE</i>) (%)	(θ)	
Neomycin Blank 10×10^{-4} 20×10^{-4} 30×10^{-4}	0.0808 0.0234 0.0176 0.0087	70.92 77.87 89.32	0.71 0.78 0.89	

Tabl	e 1 Values of Inhibition Ef	iciency and Surface	coverage for the disso	lution of SS 30	04 in 2 M H ₂ SO ₄
in pr	esence of different concentr	ations of Neomycin	obtained from mass	loss measuren	nents

Potentiodynamic Polarization Studies

Polarization results such as the values of corrosion potential $[E_{corr}]$, corrosion current densities (I_{corr}), anodic tafel slope (β_a), cathodictafel slope (β_c) surface coverage (θ) and inhibition efficiency (IE%) were calculated using polarization curves are summarized in Table 2.

Table 1 Values of Inhibition Efficiency and Surface coverage for the dissolution of SS 304 in 2 M H₂SO₄ in presence of different concentrations of Neomycin obtained from mass loss measurements

Inhibitor Conc. (M)	Weight loss (g)	Inhibition efficiency (<i>IE</i>) (%)	Surface coverage (θ)	
Neomycin				
Blank	0.0808	-	-	
10×10 ⁻⁴	0.0234	70.92	0.71	
20×10 ⁻⁴	0.0176	77.87	0.78	
30×10 ⁻⁴	0.0087	89.32	0.89	

It can also be seen from the table that corrosion current (I_{corr}) value declines with increase in the concentration of the green compound. Further it is established that increasing concentrations of neomycin improve the values of both β_a and β_c , in an unfixed manner. Hence the inhibition of corrosion by this compounds is under cathodic control, but mainly under mixed type. The inhibition efficiency (IE%) and surface coverage (θ) increases with increase in neomycin concentrations. The maximum inhibition efficiency was achieved at 30×10^{-4} M concentration. A definite relationship exists between the results obtained from mass loss and polarization studies for the above green compound.

Electrochemical Impedance Studies

The nyquist representations of impedance behavior of stainless steel 304 in 2M H₂SO₄ with and without addition of various concentrations of inhibitors are given in table 3. The table also contained the values of charge transfer resistance (R_{cl}) and double layer capacitance (C_{dl}) derived from Nyquist plots for the dissolution

of SS 304 rod in 2M H₂SO₄. It can be visualized that the values of R_{ct} was seen to increase with increase in concentration of green compound in the acid. It was found that values of C_{dl} are brought down by enhancing concentrations of neomycin in the acid medium. This can be accredited to the increasing adsorption of the inhibitor on the metal surface with increase in its concentration [33].

Inhibitor Conc. (M) Blank	$R_{\rm ct}$ (Ω cm ²) 27.2	$C_{\rm dl}$ (F cm ⁻²) 0.492	<i>IE</i> (%)	Surface coverage (θ) -	
Neomycin					
10×10 ⁻⁴	106.4	0.294	72.67	0.72	
20×10 ⁻⁴	157.7	0.202	80.8	0.81	
30×10 ⁻⁴	250.62	0.086	87.64	0.88	

Table 3	Electrochemical im	pedance parameter	rs for dissolution	ofSS 304 rod in 2 N	A H ₂ SO ₄

Hydrogen Permeation Measurements

Hydrogen can ingress into the metal during various industrial operations like melting, heattreatment, or pickling and electrochemical processes such as cathodic cleaning and electrolytic machining. Of the various sources of entry of hydrogen into the metal, pickling is one of the basic steps in electro polishing of stainless steel processes in which mineral acids areused for the removal of rust and scale. The following are the main reactions in acidic

solutions.

$$M + H_{3}O + + e^{-} \longrightarrow H_{2}O + M H_{ads}$$
(4)
where M is the cathodic metal surface. This discharge step is followed by either
$$MH_{ads} + MH_{ads} \longrightarrow 2M + H_{2}$$
(5)
$$MH_{ads} + H_{3}O^{+} + e^{-} \longrightarrow M + H_{2}O + H_{2}$$
(6)
[electrochemical desorption]

A part of the atomic hydrogen liberated throughout the pickling process passes into the metal, and the rest is evolved as hydrogen gas. Green compounds are generally added topickling baths in order to minimise the base metal attack and limit the hydrogen liberated. However, the fraction of hydrogen atoms that enters the metal produces some unfavorable effects [34] on the mechanical properties of iron/steel, such as reduction in ductility, lowering of fracture stress and loss in mechanical strength leading to embrittlement. This phenomenon is also called 'delayed failure'. It has been already pointed out that hydrogen permeation current measurement, under pickling conditions, can be a useful tool for evaluating inhibitors from the point of view of predicting the extent of hydrogen embrittlement. A similar idea has been made with regard to the airing of additivesemployed in electroplating baths for their ability to decrease hydrogen intake.

In the present study the hydrogen permeation currents are recorded in H_2SO_4 in the absence and presence of neomycin. This study has been utilized with an idea of screening the green compound for their effectiveness on the diminishing the hydrogen up take. The values of permeation current with respect to time are given in Table 4. Figure 5 shows the variation of permeation current vs time for stainless steel 304 in 2 M H_2SO_4 in the presence of neomycin.

Time	Permeation Current (µA)		
(min.)	2 M H ₂ SO ₄	Green inhibitor	
0	12.6	4.4	
5	13.2	6.5	
10	14.0	8.3	
15	15.2	10.3	
20	16.4	11.2	
25	17.2	11.2	
30	18.2	11.2	
35	19.5	11.2	

Table 4 Values of permeation current for SS 304 in2 M H₂SO₄ and in presence of green inhibitor with respect to change in time



Figure 1.Structure of Neomycin

It has been found from table that the compound lessens the permeation current .Thus a definite correlation exists between the corrosion inhibition efficiency and theextent of reduction in the permeation current of this green inhibitor. An increase in the cathodicTafel slope leads to increase in the energy barrier for proton discharge and decrease in theevolution of hydrogen. This in turn leads to lower permeation of hydrogen through themetal.

Adsorption Isotherm

The degree of Surface Coverage (θ) for different concentrations of neomycin in2 M H₂SO₄ has been calculated from weight loss, Polarization and Electrochemical Impedance studies. The obtained data was tested graphically for fitting suitable isotherm [35, 36]. A straight line was observed by plotting log (C/ θ) Vs log Cwhich confirms that the adsorption of this geen inhibitor obeys Langmuir adsorption isotherm.

The Langmuir isotherm for the adsorbed layers is given by the equation [37],

 $\begin{array}{ll}C_{\rm inh}/\theta &= 1/K_{\rm ads} + C_{\rm inh} & (7)\\ \text{Where } K_{\rm ads} \text{ is the equilibrium constant of the adsorption/desorption process. Adsorption equilibrium constant}\\ (K_{\rm ads}) \text{ and free energy of adsorption } [\Delta G^{\circ}_{\rm ads}] \text{ were calculated using the equation } [38]\\ K_{\rm ads} = 1/C_{\rm inh} \times \theta/1-\theta & (8)\\ \Delta G^{\circ}_{\rm ads} &= -2.303RT \log [55.5K_{\rm ads}] & (9) \end{array}$

Where 55.5 is the molar concentration of water in solution [39]. *R* is the gas constant, *T* is the temperature. The values of adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG^{o}_{ads}) are given in Table 5. The negative values of (ΔG^{o}_{ads}) indicated that adsorption of neomycin on SS 304 surface in acid medium is spontaneous process. It is known that values of (ΔG^{o}_{ads}) is of order 20 kJmol⁻¹ or lower indicates a physisorption, those of order of -40 kJmol⁻¹ or higher involve charge sharing or transfer from the inhibitors to the metal surface to form a co-ordinate bond, the process known as chemisorption [40-42]. The values of free energy of adsorption (ΔG^{o}_{ads}) in our experiment lies in the range -28 to -32 kJmol⁻¹, indicating that the adsorption is not a simple physisorption but it may involve some other interactions [43].

Temperature	K _{ads}	$-\Delta G^{o}_{ads}[kJmol^{-1}]$	
[K] —	Green inhibitor	Green inhibitor	
313	932	28.30	
323	1168	29.80	
333	1347	31.11	

Table 5 Gibbs free energy parameters and adsorption equilibrium constant (K_{ads}) of green inhibitor at different temperatures evaluated by mass loss method

Mechanism Of Inhibition

Inneomycin, the presence of exo oxygen which is more electronegative [-M effect] may increase electron density on the nitrogen atoms. The better performance of this compound is ascribed to the strongest adsorption of this green inhibitor through nitrogen atoms.

Conclusions

The dissolution stainless steel304 pipes were monitored and controlled in $2M H_2SO_4$ solutions at different temperatures (313–333 *K*) without and with various concentrations of neomycin, a green inhibitor by adapting chemical and electrochemical methods. The principle conclusions are:

- 1. Neomycin exhibited inhibiting properties for SS 304 corrosion in 2M H₂SO₄ effectively.
- 2. Tafel polarization plots indicated that tested green compound hehaved as mixed- type inhibitor.
- 3. Rates of corrosion obtained from the impedance measurements were in good agreement with those recorded using the Tafel polarization plots. This confirms the validity of the corrosion rates measured by the Tafel polarization plots.
- 4. Adsorption of the green inhibitor was found to follow Langmuir isotherm.
- 5. Apparent activation energies in the presence of neomycin for the corrosion of SS 304 in acid medium lie in the range 28 to -32 kJmol⁻¹, indicating that the adsorption is not a simple physisorption.
- 6. This green inhibitor brings down the ingress of hydrogen to the greater extent

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