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Corrosion Inhibition Behaviour of Mild Steel in HCL Solution in Presence of Nebicard

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ABSTRACT: Nebicard is studied for use as a low cost and ecofriendly corrosion inhibitor for mild steel in acidic environment. The corrosion inhibition effect is investigated using Tafel polarization, electrochemical impedance spectroscopy studies. The inhibitor showed 97% inhibition efficiency at 100ppm concentration of Nebicard. Potentiodynamic polarization suggests that it is a mixed type of inhibitor.

Electrochemical impedance spectroscopy techniques were also used to investigate the mechanism of corrosion inhibition. E_a and ΔG^0_{ads} were calculated to investigate mechanism of inhibition.

KEYWORDS: Adsorption, corrosion, EIS, Nebicard , mild steel

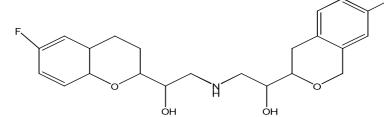
I. INTRODUCTION

Acid solutions are used in industries during various processes such as acidic cleaning, pickling and oil well acidification which generally leads to serious metallic corrosion[1-2]. It has been found that one of the best methods of protecting metals against corrosion involves the use of inhibitors. Inhibitors are added to the acid solution to minimize acid attack on metal. A large number of organic compounds including heterocyclic

compounds were studied as corrosion inhibitors for mild steel [5-6].Most of inhibitors are toxic and expensive so the research activities in recent times are geared towards developing cheap, non-toxic and environmentally safe corrosion inhibitors[7-11]. Recently, a few non-toxic compounds such as ceftriaxone, tryptamine, succinic acid, L-ascorbicacid, sulphamethaxazole, cefatraxyl, streptomycin, cefalexin, cefotaximesodium, doxycycline mebendazole, cefazolin, etc. have been investigated as corrosion inhibitors by our research group and other investigators. The present paper describe a study nebicard (nebivolol) as corrosion inhibitor for mild steel in 1N hydrochloric acid using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization techniques.

II. EXPERIMENTAL

Nebicard used in the present study was purchased from medicine shop as a trade name nebicard tablets (Bystolic tablets) and used without further purification. Nebicard is a N-F heterocyclic compound containing Two oxygen atoms, one nitrogen atoms and Two Florine atom. Hence it is expected to act as a good inhibitor. The range of the concentrations of inhibitor used for the inhibition is from 25ppm to 100



1-(6-fluoro-3,4,4a,8a-tetrahydro-2*H*-chromen-2-yl)-2-(2-(7-fluoroisochroman-3-yl)-2hydroxyethylamino)ethanol **Fig 1:** Chemical structure and IUPAC name of studied inhibitor



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Corrosion measurements:

Corrosion test were performed on the mild steel with following composition(wt%) 0.76 C, 0.192Mn, 0.012 P, 0.026 Si, 0.050 Cr, 0.023 Al, 0.123Cu and balanced Fe, were abraded successively with emery papers from 600 to 1200 grade. The specimen were washed thoroughly with double distilled water, degreased with acetone and finally dried in hot air blower. The Mild steel electrode of 8 cm \times 1 cm \times 0.025 cm sizes with an exposed area of 1cm²was used as working electrode for electrochemical study.

Electrochemical impedance spectroscopy:

The electrochemical studies were made using a three-electrode cell assembly at room temperature, using Potentiostat/Galvanostat G300-45050 (Gamry Instruments Inc., USA) Echem Analyst 5.0 software package was used for data fitting. A saturated calomel electrode was used as the reference; a platinum foil was used as counter electrode and mild steel strip as working electrode All potentials were measured w.r.f a calomel electrode (SCE) i.e. reference electrode. Tafel curves wereobtained by changing the electrode potential automatically from -0.25 V to +0.25 V versus open corrosion potential at a scan rate of 1.0 mVs-1. EIS measurements were performed under potentiostatic conditions in a frequency range from 100 kHz to 0.01 Hz, with amplitude of 10mV AC signal. All experiments were measured after immersion period for 30 min of Mild steel in 1 M HCl in absence and presence of different concentration of inhibitor.

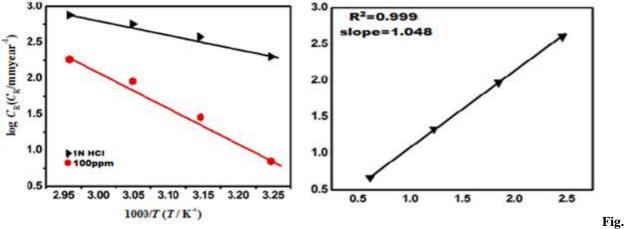
III. RESULTS AND DISCUSSION

Adsorption isotherm-

In order to understand the adsorption behaviour of inhibitors on Mild steel surface, the experimental data were tested on several adsorption isotherms. Langmuir isotherm was found to be the best fit and given by following equation:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}}$$
(1)

where, K_{ads} is the equilibrium constant of the adsorption-desorption process, θ is the degree of surface coverage and C_{inh} is molar concentration of inhibitor A straight line was obtained on plotting (C/θ) vs C for Langmuir isotherm show in Fig.2, with a slope value of 1.048



2(a) Adsorption isotherm plots in absence and presence of 100 ppm concentration of for log C_R vs. 1/T,(b),Langmuir adsorption isotherm

The standard free energy of adsorption (ΔG^0_{ads}) and the values of equilibrium constant (K_{ads}) are calculated with the following equation,



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 $\Delta Gads = -RT \ln \left(55.5Kads \right) \tag{2}$

The negative values of ΔG_{ads} indicate that adsorption of the inhibitors on the metal surface is spontaneous. It is reported that values(ΔG_{ads}^{0}) around- 20 kJ mol⁻¹ suggests physisorption and around- 40 kJ mol⁻¹ suggests chemisorptions. The value 55.5 in the above equation is the concentration of water in solution in mol/lit. The calculated values of ΔG_{ads}^{o} are in range of -39.84 to-41.74 kJ mol⁻¹ indicating that the adsorption of the inhibitor on Mild steel surface. Is close to chemisorptions.

Kinetic and thermodynamic considerations:

Thermodynamic parameters are important to study the inhibitive mechanism of the inhibitor. The dependency with of corrosion rate at temperature can be expressed by Arrhenius equation:

$$\log(C_{\rm R}) = \frac{-E_{\rm a}}{2.303RT} + \log\lambda \tag{3}$$

The apparent activation energy and pre-exponential factors can be calculated by linear regression between $\log C_{\rm R}$ and 1/T, and the results were shown in Fig. 3. The plots obtained are straight line and the slope of each straight line gives its apparent activation energy. $E_{\rm a}$ values for blank is 38.14 kJ mol⁻¹ and in the presence of inhibitors is 92. 40 kJ mol⁻¹. It was observed that the values of apparent activation energy $E_{\rm a}$ is higher in presence of inhibitor than in its absence, which indicates that the energy barrier for the corrosion reaction increases in presence of inhibitor.

Electrochemical measurements:-

Potentiodynamic polarization measurement

The polarization curves in the absence and presence of different concentrations of Nebicard drug are shown in Fig. 3a, and corresponding parameters like Corrosion potential (E_{corr}), corrosion current densities (I_{corr}), anodic and cathodic slopes (β_a and β_c) are listed in Table 1. It can be seen from the results that shift in *E*corr values are less than 85 mV [12] and towards negative direction which suggests that Nebicard drug behave as mixed type of inhibitors but predominantly acts as cathodic. The electrochemical data reveals that the value of *I*corr decreases in the presence of different concentrations of Nebicard drug.

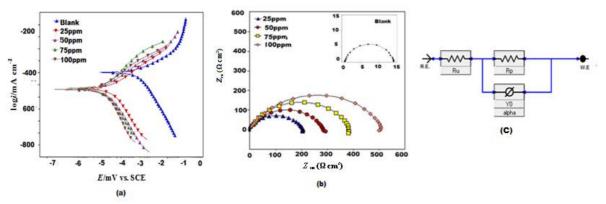


Fig. 3(a), polarization polarization,(b) Nyquist plots with(c) equivalent circuit in used for analysing the electrochemical data of mild steel in 1N HCl in absence and presence of different concentrations of Nebicard drug The inhibition efficiencies were calculated from I_{corr} values by following equation.



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Inhibitor	EIS data				Tafel DATA				
conc. ppm	$\frac{R\alpha}{(\Omega \text{ cm}^2)}$	Y_0 (µF cm ⁻²)	n	η%	- Ε coa mV vs. SCE	icon μA cm ⁻ 2	₿a mV/dec	<u>ßc</u> /mV/ dec	μ _p %
-	12.291	299	0.8	-	-448	1590	57.2	141.5	-
25	200.445	140	0.81	93.8	-516	122	77.2	141.7	92
50	288.844	143	0.8	95.7	-519	69.1	85.2	130.4	95
75	382.852	68	0.8	96.7	-516	38.8	66.7	91.2	96
100	495.13	144	0.78	97.5	-518	34	71.1	94.7	97

Table 1: Electrochemical parameters derived from EIS and potentiodynamic polarization in absence and presence of different concentrations of Nebicard drug

$$\eta \% = \left(1 - \frac{I_{\text{corr(i)}}}{I_{\text{corr}}}\right) \times 100$$
⁽⁴⁾

where I_{corr} and $I_{corr(i)}$ are the corrosion current density of mild steel in absence and presence of inhibitor.

Electrochemical impedance spectroscopy (EIS)

The EIS curves for mild steel in the absence and presence of Nebicard drug at different concentrations are shown in Fig. 3b. The calculated impedance parameters are given in Table 1. Nyquist plots revealed that the diameter of semicircles loop is large as compared to blank, also with increases in concentrations of inhibitors the diameter of loop increases, which suggests that Nebicard drug act as effective corrosion inhibitor for Mild steel .The analysis of Nyquist plots reveal that the corrosion process is mainly charge transfer controlled.[13].The Equivalent circuit model shown in Fig. 3c, was used to analyze the Nyquist curves which consists of R_s (solution resistance), CPE (constant-phase element) parallel to the R_{ct} (charge transfer resistance)[14]. The inhibition efficiency is calculated using charge transfer resistance (R_{ct}) as follows [15].

$$\eta\% = \left(1 - \frac{R_{ct}}{R_{ct(i)}}\right) \times 100$$
⁽⁵⁾

The double layer capacitance was calculated by using following equations [16]

$$C_{dl} = \frac{1}{\omega R_a} = \frac{1}{2\pi \int_{max} R_a}$$

(6)

Table 1, reveals that the increase in concentration of inhibitors causes increase in R_{ct} values and corresponding decrease in C_{dl} .

VI. CONCLUSIONS

Nebicard drug acts as good inhibitor, EIS studies showed that diameter of capacitive loops and charge-transfer resistance (R_{ct}) increased with increase in concentration. Polarization studies indicate that Nebicard drug are mixed



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type inhibitor predominating cathodic . The adsorption of inhibitor molecules on the Mild steel surface in 1N HCl solution follows Langmuir adsorption isotherm. The negative values of ΔG°_{ads} show the spontaneity of the adsorption.

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