Corrosion Inhibition of Mild Steel in 1 M HCl and 0.5 M H₂SO₄ by Natural Product Extract - A Comparative Analysis by Electrochemical Studies

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ABSTRACT - *Potentiodynamic polarization measurements and electrochemical impedance spectroscopy were used to study the inhibition effect of Citrus aurantiifolia leaves on the corrosion of mild steel in 1.0 M HCl and 0.5 M H_2SO_4 solutions. The results obtained show that the inhibition was found to increase with increasing concentrations of the plant extract. Polarization curves revealed that the inhibitor acts as mixed type inhibitor and inhibition efficiency follows the order: HCl> H_2SO_4.*

Keywords: Mild steel, Corrosion inhibitors, Electrochemical studies, Acid Corrosion

1, INTRODUCTION

Acids are used to remove oxides, shop-soil and other contaminants from metal surfaces. Acids are also used for derusting and pickling, the cleaning of refinery equipment, and the removal of calcareous deposits from boilers, radiators of vehicles, pipelines carrying water or petroleum products, heat exchangers etc., [1] Both HCl and H_2SO_4 are frequently used in the above industrial activities. Inhibitors are generally used in these processes to control the metal dissolution as well as acid consumption. Use of inhibitors is an important task in the protecting of metals from corrosion. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products [2]. The recent trend is towards developing environment friendly inhibitors. Most of the natural products are non – toxic, bio – degradable and readily available in plenty. Various parts of plants – seeds, fruits, leaves, flowers etc., have been used as corrosion inhibitors [3]. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media. [4-15]. Our previous works [16-17] reported a successful use of natural product as corrosion inhibitor for mild steel in acidic medium. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

2, Experimental

Rectangular samples of area 5×1 cm^2 have been cut from a large sheet of mild steel. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with 400 grade emery papers, degreased in a solution of non-toxic detergent, washed with distilled water, dried, weighed and stored in desiccators for further use.

For the present study, natural product of *Citrus aurantiifolia* leaves (C.A.L) is used as corrosion inhibitor for mild steel in 1 M HCl and 0.5 M H_2SO_4. The leaves were collected from a farm in Duraiyur, Trichy. The leaves were collected, shade dried and powdered. 5% extract was prepared by refluxing 25 g of powdered dry leaves and seeds in 1 M HCl and 0.5 M H_2SO_4 for 3 hours and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500 mL using the same acid.

2.1 Potentiodynamic Polarization Measurements

Potentiodynamic polarization studies were carried out using Solartron 1280 B. The cell of the polarization studies was a glass beaker containing the aerated unstirred test solution with a platinum electrode as the counter electrode, a saturated calomel electrode as reference electrode and the mild steel electrode as the working electrode. 100 mL of 1 M HCl and 0.5 M H_2SO_4 in absence and in presence of different concentrations of the inhibitor was taken in an electrochemical cell. The polished electrode with an exposed area of 1 cm^2 was then introduced. The electrode was placed at -0.2 mV/s towards the anodic direction in the Tafel extrapolation. Applied potential vs. current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current (I_{corr}). In anodic and cathodic plot, the slope of the linear portion gives Tafel constants, b_a and b_c respectively. According to the Stern – Geary equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$I_{corr} = \frac{b_a \times b_c}{2.303(b_a + b_c)} \times \frac{1}{R_p}$$

where, R_p is polarization resistance.

2.2 Impedance studies

Impedance measurements were carried out at each corrosion potential. An ac sine wave of 10 mV amplitude was applied to the electrode. The frequency which is varied from 10 KHz to 100 MHz was superimposed at the open circuit potential. The results are presented in the form of Nyquist plots. All the measurements were presented in the corrosion potential.

In Impedance method, the charge transfer resistance (R_{ct}) is obtained from the plots of Z' Vs Z'' (real part Vs imaginary part; Nyquist plot). The value (R_p+ R_s) corresponds to the point where the plot cuts Z axis to the point where the semicircle cuts the Z axis at high frequency. The difference gives the R_p values, which were substituted in the Stern-Geary equation to get I_{corr},

$$I_{corr} = \frac{b_a \times b_c}{2.3 (b_a + b_c) R_{ct}}$$

The b_a and b_c values were experimentally obtained as mentioned in the case of linear polarization for each system.

3, Results and Discussion

3.1 *Potentiondynamic Polarisation results*

The various electrochemical parameters calculated from Tafel plot (Fig 1) are given in Table 1. The lower corrosion current density (I_{corr}) values in the presence of inhibitor without causing significant changes in corrosion potential (E_{corr}) suggests that the compound is a mixed type inhibitor (i.e., inhibit both the anodic and cathodic reactions) and are adsorbed on the surface thereby blocking the corrosion reaction [18]. In all concentrations, b_a is greater than b_c suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

TABLE – 1: ELECTROCHEMICAL PARAMETERS FOR MILD STEEL IN 1 M HCl AND 0.5 M H₂SO₄ WITH VARIOUS CONCENTRATIONS OF C.A.L

S.No	Conc (%V/V)	$-E_{corr}$ mV		I_{corr} μAcm^{-2}		b_a mV/dec		b_c mV/dec		I.E (%)	
		1 M HCl	0.5 M H₂SO₄	1 M HCl	0.5 M H₂SO₄	1 M HCl	0.5 M H₂SO₄	1 M HCl	0.5 M H₂SO₄	1 M HCl	0.5 M H₂SO₄
1	Blank	522.29	543.02	4.521	3.393	168.96	260.01	121.54	169.36	-	-
2	0.005	516.52	546.28	5.555	4.527	206.21	321.59	140.51	200.64	-22.87	-33.42
3	0.05	526.49	528.15	2.877	0.791	135.71	164.67	106.03	99.86	36.36	76.66
4	0.15	516.85	521.49	0.859	0.501	126.31	160.94	100.47	92.69	80.99	85.21
5	0.5	511.78	518.57	0.311	0.321	130.07	182.34	90.71	82.89	93.10	90.52
6	2.5	502.15	70.27	0.094	0.159	140.31	210.84	81.79	70.50	**97.91**	**95.30**

Fig 1
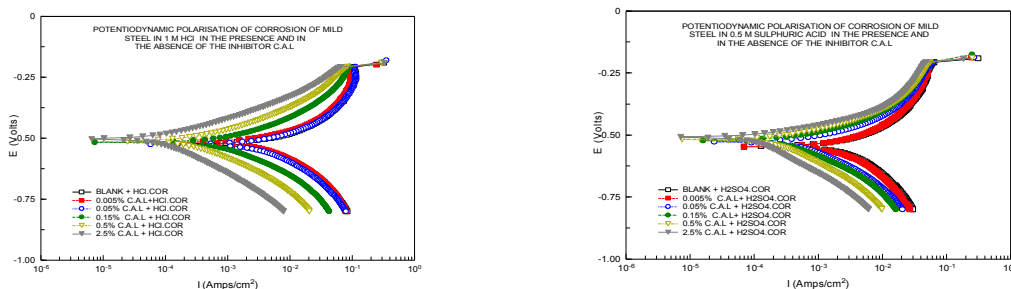
3.2 Electrochemical impedance spectroscopy results

Impedance diagram (Nyquist plot) obtained for mild steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of various concentrations of the inhibitor is depicted in Fig 2. They are perfect semicircles and this was attributed to charge transfer reaction [19]. Impedance parameters derived from Nyquist plots are tabulated in Table 2. It can be seen that as the concentration of inhibitor increases, C_{dl} values decrease. Decrease in C_{dl}, which can result from an increase in thickness of electrical double layer, suggests that the inhibitor molecule function by adsorption at the metal- solution interface [20].

TABLE – 2: IMPEDANCE PARAMETERS FOR THE CORROSION OF MILD STEEL IN 1 M HCl AND 0.5 M H_2SO_4 CONTAINING DIFFERENT CONCENTRATIONS OF C.A.L
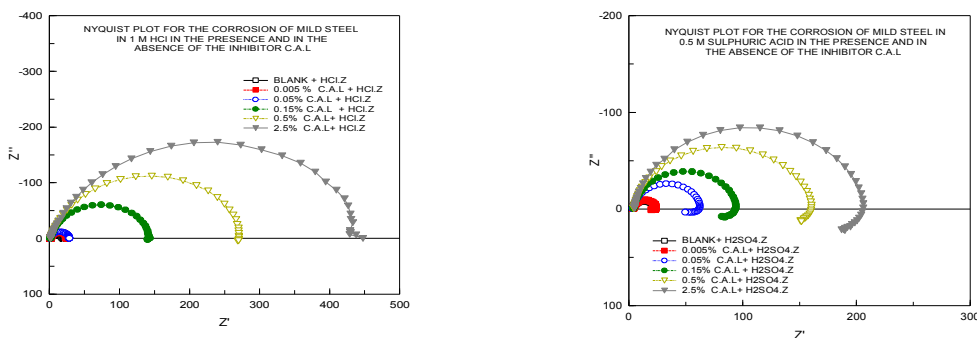
Fig 2

TABLE – 3: COMPARISON OF R VALUE BY ELECTROCHEMICAL STUDIES

| Type of electrochemical studies	r

| Potentiodynamic polarisation method	0.93
Impedance Method	0.87

3.3 Explanation for inhibition

The acid extracts investigated in the study are organic in nature and found to contain the following compounds. The probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the extract. The inhibition may be due to the adsorption of phytochemical constituents present in the extract through oxygen atoms on to the surface of the metal.
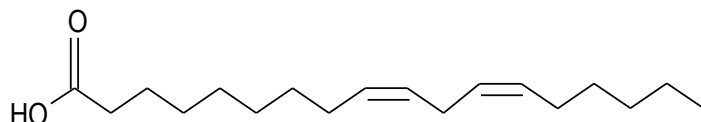
Oleic acid
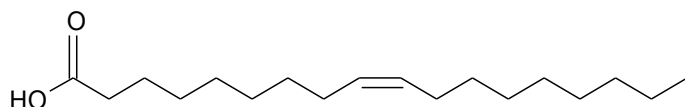
Xanthyletin
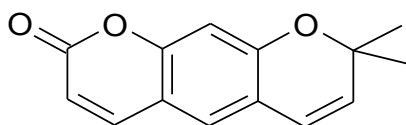
Linoleic acid

The inhibitive ability of C.A.L in HCl is comparatively more than in H_2SO_4. This is due to the fact that Cl^- have stronger tendency to adsorb than SO_4^{2-} ions [21] and the electrostatic influence on the inhibitor adsorption may be the reason for an increased protective effect in halide containing solution [22]. Though by the comparative studies by electrochemical method it is concluded that the inhibition efficiency is better in HCl than in H_2SO_4, Inspecting Table 3, r value suggests both are equal.

4, Conclusion

The natural extract of the inhibitor was found to be effective inhibitor in the acidic medium. The results obtained from the polarization study revealed that the extract under study behaved as a mixed type of inhibitor. From the comparative studies it is concluded that the inhibition efficiency is better in HCl than in H_2SO_4.

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