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Der Pharma Chemica, 2010, 2(1): 287-294
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Corrosion inhibitor-A plant extract

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Abstract

The efficacy of an acid extract of leaves of *Sida rhombifolia.L* as corrosion inhibitor for mild steel in 1M phosphoric acid medium, was carried out using weight loss measurements, polarization and electrochemical impedance spectral studies. Experiments are performed by varying immersion period, concentration of the inhibitor and temperature. The results showed variation in inhibition performance of the inhibitor with varying concentration, immersion time and temperature. The maximum efficiency was found to be 97.48% at 1 %(w/v) concentration of the inhibitor for the immersion period of 24 hours. Langmuir and Temkin were tested to describe the adsorption behavior of inhibitor on the mild steel surface. Potentiodynamic polarization study clearly revealed that inhibitor acts as a mixed type of inhibitor. The results of the electrochemical impedance study showed a decrease in double layer capacitance as the adsorption of inhibitor caused structural change at electrode-solution interface.

Key words: Corrosion inhibition, *Sida rhombifolia.L*, adsorption isotherms, Potentiodynamic polarization, electrochemical impedance.

Introduction

Corrosion of the mild steel and alloys is a major issue for many industries because of the chemical environment of the industrial processing. In many industries, acids such as hydrochloric, sulphuric or phosphoric are widely used for pickling, descaling, acid cleaning, oil well acidising, etc. The acids damage the materials under treatment. In this kind of situation, organic and inorganic inhibitors are used to reduce the corrosive property of acids [1-3]. Some of organic inhibitors available are considered to be very toxic and expensive. Therefore, attention has been focused on 'environment friendly green inhibitors' of plant origin, which are inexpensive, readily available and are renewable sources of materials [4-5].The protection of metals against corrosion in Phosphoric acid has been the subject of much interest since it has been used in many industrial processes, especially in fertilizer production. Some investigations have also been done on the inhibition of mild steel in phosphoric acid using synthetic inhibitors [7-9], but little works appear to have been done using naturally occurring substances in phosphoric acid as corrosion inhibitors for mild steel [10-11]. Therefore, an attempt has been made in the present study to evaluate the inhibitory effect of *Sida rhombifolia.L* as a green corrosion inhibitor on mild steel in phosphoric acid.

Results and Discussion

Weight loss on inhibitor application

Table 1: Immersion period and inhibition efficiency of Sida *rhombifolia.L*

Immersion Period	Inhibition efficiency			
	0.01	**0.1**	**0.5**	**1**
1	64.62	84.14	91.71	92.16
3	78.2	89.48	94.59	95.6
7	80.7	91.5	96.4	97.18
24	43.1	87.6	96.88	97.48

From Table 1 it is evident that the inhibition efficiency increases for various immersion periods. Further, inhibition efficiency increases for immersion period of 24 hour at higher concentrations of 0.5% and 1%. It is noted that the maximum efficiency of 97.48 % is reached at 1% concentration of inhibitor for the immersion period of 24 hour. However a decrease in inhibition efficiency is found for lower concentrations of 0.01% and 0.1% at 24th hour. This may be due to decrease in concentration of active inhibitor molecules in the corrosion medium.

Effect of temperature

Corrosion inhibition of Sida rhombifolia extract on mild steel corrosion in the phosphoric acid was studied at various temperatures. The data is given in Table 2.

Table 2: Inhibition efficiency at various temperatures in the presence of Sida *rhombifolia.L*

Conc. (%) (w/v)	Inhibition efficiency (%)				
	303K	**313K**	**323K**	**333K**	**343K**
0.01	41.6	61	64.6	45.8	38
0.1	84.1	84.5	87.2	72	54.7
0.5	91.7	93	94.2	91	87.9
1	92.2	95.3	95.6	91.2	90.5

It is clear from Table 3 that the inhibition efficiency increases with increasing temperature (303-323K). In fact there is a linear regular trend in inhibition efficiency up to 323K. It is because the increase in temperature accelerates the chemisorptions of the inhibitor on the metal surface. Optimum temperature is 323K. However there is a decrease in efficiency when the temperature rises (333 and 343 K). There may be a competition between adsorption over desorption of the inhibitor and hence inhibition efficiency decreases.

Thermodynamic data

Thermodynamic parameters are essential to explain the role of inhibitor in bringing down the corrosion rate of mild steel in acid medium. Various thermodynamic parameters such as Activation energy (Ea), Enthalpy of adsorption (ΔH_{ads}) and Entropy of adsorption (ΔS_{ads}) are calculated and are given in Table 3.

Table 3: Thermodynamic parameters for Sida rhombifolia

Parameters	**Percentage concentration(w/v)**				
	blank	**0.01**	**0.1**	**0.5**	**1**
-Ea kJ/mol	46.6769	48.9286	48.8118	48.0785	48.6614
-ΔH_{ads} kJ /mol	44.0174	46.2691	46.1925	50.8146	46.045
-ΔSads kJ/mol	0.03693	0.03167	0.04329	0.0366	0.0536

The data shows that the activation energy, Ea for the inhibited system is higher than that in the free acid. The higher activation energies imply a slow dissolution of iron metal. The thermodynamic enthalpy function, ΔH_{ads} is negative confirms the exothermic behavior of the adsorption process and indicates strong adsorption as the value of ΔH_{ads} is greater than 40 k $Jmol^{-1}$. The negative values of ΔS_{ads} imply that the activated complex in the rate determining step represents association rather than dissociation.

Adsorption isotherms

Adsorption isotherm values are important to explain the mechanism of corrosion inhibition of organo - electrochemical reactions. The most frequently used isotherms are Langmuir and Temkin.

Table 4: Langmuir adsorption isotherm values for *Sida rhombifolia.L* at different temperatures

Temp in K	**slope**	**intercept**	**R^2**	**(1/Y)**	**-ΔG_{ads} kJ/mol**
303	0.5443	0.981	0.9772	1.837	17.4196
313	0.4589	1.1356	0.9293	2.179	18.2354
323	0.4628	1.2058	0.9471	2.208	18.8199
333	0.4985	0.9258	0.9839	2.006	19.40
343	0.536	0.7924	0.927	1.866	19.98

Table 5: Temkin adsorption isotherm values for *Sida rhombifolia.L* at different temperatures

Temp in K	**Slope**	**Intercept**	**R^2**	**‘a’**
303	0.2625	0.9687	0.9649	8.7733
313	0.1745	0.9739	0.9799	13.198
323	0.1571	0.9801	0.9586	14.659
333	0.2391	0.9472	0.9805	9.632
343	0.2807	0.9111	0.9515	8.204

In Tables 4 and 5, R^2 is regression coefficient. 1/Y (Table 4) is the number of active sites occupied by inhibitor and ‘a’ (Table 5) is molecular interaction parameter.

The regression values (R^2) are greater than 0.9 in Table 4 and 5, show that the data obtained for the inhibitor fits well in Langmuir and Temkin adsorption isotherms. Since it obeys Langmuir adsorption isotherm, it implies monolayer adsorption of inhibitor. As the slope values of Langmuir adsorption isotherm in Table 4 are slightly deviate from the value of one, the experimental data were fit into El-awady’s thermodynamic model to find number of active sites (1/Y) occupied by the inhibitor. In the present study, Table 4 shows 1/Y as nearly equal to two, showing that two of the water molecules adsorbed on the metal surface are replaced by two of the inhibitor molecules and get adsorbed on the corroding site of metal surface thus reduces the number of active sites involved in corrosion, which can be represented in the equation (1)

$$\mathrm{Fe\,(H_2O)_2 + inhibitor \rightarrow Fe(inhibitor)_2 \; +2\,H_2O} \qquad (1)$$

The molecular interaction parameter, ‘a’ obtained from Temkin adsorption isotherm is very high and hence shows attractive force existing between mild steel surface and the inhibitor. The adsorption of the inhibitor on the metal surface leads to high degree of surface coverage and hence shows better inhibitive property.

Potentiodynamic Polarization Study

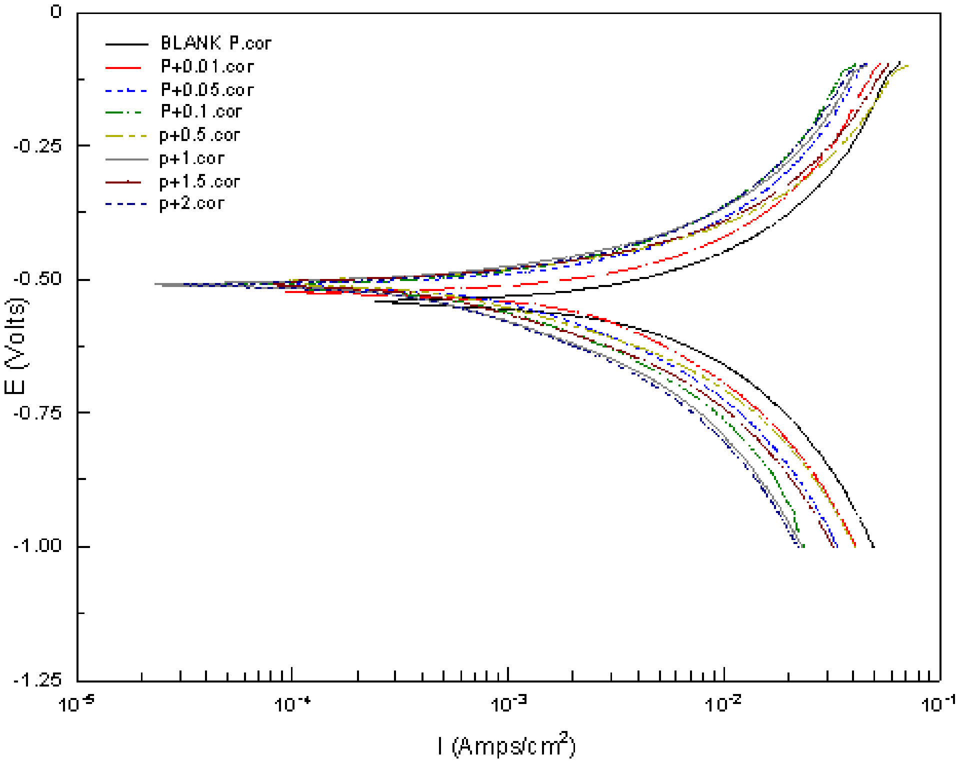


Figure 1 : Potentiodynamic polarization plots *Sida rhombifolia*.L.

It is obvious from the Fig.1, that in the presence of the inhibitor the curves are shifted towards lower current regions, showing the inhibition tendency of inhibitor.

Table 6: Potentiodynamic Polarization Parameters for S*ida rhombifolia.L*

Conc%	-Ecorr mV	Icorr µ(amp/cm^2)	-ßa mV/dec	-ßc mV/dec	Rp Ohms/cm^3	%I .E
Blank	534.15	9474.4	633.26	496.09	13.243	-
0.01	524.34	4738.1	271.91	399.24	10.934	49.0
0.1	511.85	2187.6	269.38	193.59	22.357	76.9
0.5	504.87	1151.1	231.12	164.62	34.744	87.8
1.0	506.81	683.35	252.99	154.7	48.079	92.79

The Potentiodynamic polarization parameters and inhibition efficiency are presented in Table (6). In the presence of the inhibitor, Icorr values decreases, indicating the inhibitive nature of the inhibitor. Both the anodic and cathodic Tafel slopes, namely ßa and ßc respectively are varying from the blank values, indicating again the mixed mode of inhibition. That is the inhibitor retards both the anodic reaction of mild steel dissolution and cathodic reaction of hydrogen ion reduction.

Electrochemical impedance spectroscopy

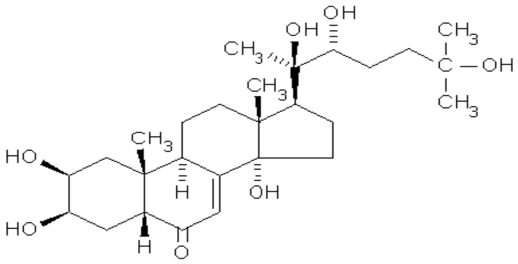
The electrochemical impedance parameters (R_{ct} and C_{dl}) were established from the Nyquist Plots and are given in Table 7. Values of charge transfer resistance (R_{ct}) increase with increasing inhibitor concentration, is attributed to high resistance shown by the adsorbed inhibitor present at the metal – solution interface. Similarly, the decrease in double layer capacitance (C_{dl}) is attributed to increase in thickness of electrical double layer due to adsorption of inhibitor. The charge transfer resistance, R_{ct} and double layer capacitance (C_{dl}) is much higher than those in free acid.

Table 7 Impedance Parameters for *Sida rhombifolia.L*

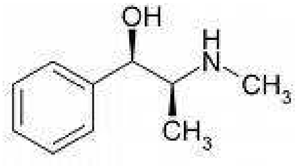
conc.	**R_{ct} ohm cm^{-2}**	**C_{dl} µF**	**%I.E R_{ct}**	**%I.E C_{dl}**
Blank	11.413	94.01	-	-
0.01	23.352	75.573	51.12	19.56
0.1	122.66	16.678	96.77	82.75
0.5	353.81	16.473	97.74	82.5
1	386.04	12.183	97.74	87.75

Mechanism of inhibition

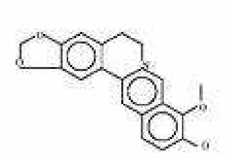
Literature survey revealed the presence of following principle constituents in the leaves extract of *Sida rhombifolia.L* [12-14]. The probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the extract.



Hydroxy Ecdysone



Ephedrine.



Sida rhombifolia alkaloid

Figure 4: Phytochemical constituents in *Sida rhombifolia.L*

The anodic inhibition may be due to the adsorption of principle phytochemical constituents present in the extract through nitrogen atom in Ephedrine /or ring oxygen atom in Rambiffolina alkaloid and /or oxygen atoms of –OH group in Hydroxy Ecdystone and forms a protective coating on the metal surface, thus prevents the contact between the metal and corrosive acid. The protonated species of the principle constituents may compete with H^+ ion reduction and may control the cathodic reaction.

Materials and Methods

Preparation of specimen

Experiments were performed with commercial grade mild steel sheets available in the local market and the elemental analysis was carried out using vacuum emission spectrometer of model BAIRD-DV4. The weight percentage composition was found to be C = 0.039, S = 0.028, Si = 0.19, P = 0.017, Mo = 0.006, Ni = 0.012, Mn = 0.272, Cr = 0.021 and Fe = 99.415. The sheets were mechanically pressed and cut into samples of size 1 X 5 x 0.2 cm^3. These samples were polished with different grades of emery papers, degreased with acetone, washed with double distilled water finally dried and kept in desiccators for further study.

Preparation of plant extract

Sida rhombifolia L. leaves were collected in and around N.G.M.College campus in Pollachi, shade dried and ground to powder. 50 g of the powder was refluxed in one litre of 1M phosphoric acid for 3 hours and kept overnight. The extract was filtered and the volume of the filtrate was made up to 1000 ml using the same acid and stored. From this stock solution, test solutions were prepared at concentrations ranging from 0.01 to 1 %.

Weight loss measurement

The weight loss measurements enable us to illustrate the importance of the environment in the process of rusting. Experiments were carried out at room temperature as well as at elevated temperatures as temperature can modify the interaction between the mild steel and the acid medium in the presence of inhibitor. The mild steel specimens were pre-weighed using electronic balance M-220D Denver. The mild steel specimens were suspended in triplicate with the help of a glass hook in 100 ml of 1 M phosphoric acid solution in the absence and presence of inhibitor at different concentrations under varying immersion times (1h, 3h, 7h and 24 h) at room temperature. The specimens were removed after specified time intervals, dipped in sodium carbonate for neutralization of residual acid remaining on the surface of the specimen. The specimen were washed with distilled water, dried, and reweighed. The experiment was conducted at higher temperatures as done at room temperature for a period of 1hour in the presence and absence of inhibitor in 1M phosphoric acid using the thermostat set to higher temperatures of 313K, 323K, 333K and 343K.

Electrochemical measurements

The potentiodynamic and EIS studies were carried out using frequency response analyzer Solatron 1280B and IBM personal computer which automatically controls and measures polarization and impedance. The data were analyzed using computer software like corrware and Z plot. Electrochemical measurements were carried out in a three electrode cell assembly. The working electrode was mild steel specimen, which was polished and lacquered to expose an area of 1 X 1 cm^2. A saturated calomel electrode and platinum electrode were used as reference electrode and counter electrode respectively. 100 ml of phosphoric acid solution containing varying concentration of inhibitor was used as electrolyte. The electrode is kept at ±400mV cathodic to its open circuit potential with the scan rate of 2mV/s.

Conclusion

Sida rhombifolia is identified as a suitable corrosion inhibitor for mild steel in 1M H_3PO_4 over a wide range of concentrations from 0.01–1%. Inhibition efficiency increases for longer immersion periods at higher concentrations. Similarly inhibition efficiency increases up to 323K. ΔH_{ads} is negative, confirms the exothermic behaviour of the adsorption process. ΔG_{ads} is negative, shows adsorption of inhibitor on the metal surface as a spontaneous process. ΔS_{ads} is negative, shows the reaction to be association in the rate determining step rather than dissociation. The adsorption of active components of inhibitor obeys Langmuir and Temkin adsorption isotherms confirm that the inhibitor acts via a simple adsorption. Polarization studies indicate the inhibitor is of mixed type.

Acknowledgement

The authors sincerely thank the authorities of Avinashilingam University for Women, Coimbatore, Tamilnadu, India for providing the facilities to carry out the study.

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