Asian Journal of Chemistry Vol. 22, No. 1 (2010), 408-414

Corrosion Inhibition of Mild Steel by Ecofriendly Extract of *Croton sparciflorus*

P.K. KASTHURI* and A. ARULANANTHAM†
Department of Chemistry, PPG Institute of Technology, Coimbatore-641 035, India
E-mail: kasthuriiii@rediffmail.com

The acid extract of *Croton sparciflorus* containing bio active ingredients have been used as corrosion inhibitor for mild steel in 1 M HCl. The inhibitor efficiency calculated using weight loss, potentio-dynamic polarization and impedance methods has been found to be effective inhibitor. The effect of temperature on the corrosion behaviour of mild steel indicated that inhibition increased with increasing temperature. It follows Temkin adsorption isotherm. Polarization and impedance studies revealed that the inhibitor was mixed type and may form a complex with the metal surface.

Key Words: Adsorption, Bioextract, Corrosion inhibition, Ecofriendly inhibitor, Mild steel.

INTRODUCTION

The corrosion inhibition of iron using large number of bio extracts having hetero atoms is found to have higher basicity and electron density. There are numerous naturally occurring substances like *Enicostemma axillare, Adhatoda vasika, Acalypha indica*[1-3] have been evaluated as effective corrosion inhibitors. Due to the tremendous increase in industrial activities hydrochloric acid is widely used in pickling and descaling. Hence hydrochloric acid was chosen for the present study. Mild steel is a material of choice for fabrication of various reaction vessels, pipes, tanks, *etc*. in most of the chemical industries but it suffers from severe corrosion in aggressive environments. In the present investigation an attempt has been made to evaluate acid extract of *Croton sparciflorus* as acid corrosion inhibitor for mild steel. *Croton sparciflorus* is a member of *Euphorbiacea*. This plant is used in India as an antiseptic and styptic and is considered to be a troublesome weed. Various alkaloids and 12, 13-diesters of the poly functional diterpene phorbol, norsinoacutine[4] have been isolated from this plant. Phytochemical screening test of the acid extract indicated the presence of an alkaloid, keto terpenoids and saponins. Hence, it was selected to study its corrosion inhibition action on mild steel in 1 M HCl medium.

†Department of Chemistry, Government College of Technology, Coimbatore-641 013, India.

EXPERIMENTAL

Reagent grade acid was used for preparation of acid extract of *Croton sparciflorus*. Five percent of stock solution of the extract was prepared by refluxing 50 g of the dried and crushed leaves of *Croton sparciflorus* with 1000 mL of 1 M HCl for 3 h and leaving it overnight. Next day the filtrates volume was made up to 1000 mL using the same acid.

Weight loss measurement: Mild steel strips of size 1 cm × 5 cm × 0.2 cm with small hole of 2 mm diameter near the upper edge of the specimens were polished with buffing and washed with Clark solution (1 L of HCl + 50 g stannous chloride + 20 g antimony trioxide) then rinsed with distilled water and finally dried with filter paper and stored in a desiccator. The coupons were weighed and fully immersed in 100 mL of acid solution with the help of glass hooks with and without inhibitor at different concentrations (0.05, 0.1, 0.2, 0.3, 0.5, 0.7 and 0.9 %). Experiments were carried out in 1 M HCl at 298 K for 0.5, 2, 4, 6, 8, 24 and 48 h, respectively. The influence of temperature on the corrosion of mild steel has also been studied at 5 different temperatures ranging from 298 to 343 K in the absence and presence of the inhibitors at different concentrations for 0.5 h.

Electrochemical studies: Potentiodynamic polarization and impedance studies were carried with the help of IM6 BAS-ZAHNER Instrument with Thalas software. For polatization study platinum foil and a saturated calomel electrode were used as auxiliary and reference electrodes respectively. Electrochemical studies of mild steel in 1 M HCl was carried out in the absence and presence of the inhibitor of different concentrations (0.05, 0.2, 0.3, 0.5 and 0.7 %). The various kinetic parameters such as I_{corr}, E_{corr}, bc and ba have been obtained from the polarization curves. The inhibition efficiency was calculated from the I_{corr} values using the following relationship.

$$IE\ \% = \frac{I_{corr}(blank) - I_{corr}(inh)}{I_{corr\,(blank)}} \times 100$$

Impedance measurements were carried out at corrosion potential with the AC amplitude of 20 mV for the frequency range of 10 kHz to 10 MHz. The real and imaginary parts of the impedance were plotted in Nyquist and Bode plots. From the plots charge transfer resistance (R_{ct}) and inhibition efficiency were calculated.

$$IE\ \% = \frac{R_{ct\,(inh)} - R_{ct\,(blank)}}{R_{ct(inh)}} \times 100$$

RESULTS AND DISCUSSION

Weight loss measurement: Table-1 shows the values of corrosion rate (CR), percentage of inhibition efficiency (IE) obtained from weight loss measurement for different concentration of the extract in 1 M HCl at 298 K for 6 h.

$$IE\ \% = \frac{(W_u - W_i)}{W_u} \times 100$$

where W_u and W_i are the weight losses in the absence and presence of inhibitor respectively. As can be seen in Table-1 the percentage of inhibitor efficiency increases with increase in the extract concentration, over the entire concentration range studied, in all cases. The maximum inhibition efficiency of the extract was found to be 99.12 % at a concentration of 0.7 % and further increase in concentration did not cause any appreciable change in the performance of inhibitor. The results seem to be consistent more or less with an inhibition mechanism involving chemisorptions of some phytochemical ingredients in the leaves extract of *Croton sparciflorus*[5]. The maximum inhibition efficiency was observed for 6 h of contact at 298 K. The effect of temperature in the range 298 to 343 K on the corrosion of mild steel in 1 M HCl in the absence and presence of the extract was also studied. Table-2 shows the values of corrosion rate (CR), percentage of inhibition efficiency (IE) obtained from weight loss measurement for different concentration of the extract in 1 M HCl at 323 K. The inhibition efficiency was increased with increasing temperature. Considering the influence of temperature on the behaviour of acid extract of *Croton sparciflorus*, it is noted that the inhibition efficiency increased up to 323 K and then slightly decreased, since chemisorptions increases with temperature due to the strengthening of chemical bonds. As a result inhibition efficiency increases with temperatures up to the temperature at which decomposition of the inhibitors occurs. This indicates that the chemical adsorption for the inhibitor on the metal surface. The maximum inhibition efficiency was found to be 96.59 % at 323 K for 0.7 % concentration of the extract. The inhibitive action may be explained by the adsorption of the extract molecules through oxygen center of OH or CO functional groups of the active ingredients by the complex formation on the corroding surface. To explain the nature of the adsorption of the inhibitor, adsorption isotherm model of Temkin was employed[6].

$$\text{Temkin Isothrem} = \exp\left(-2a\theta\right) = KC$$

where C is the concentration of the inhibitor and θ is the surface coverage. Fig. 1 represents the θ against inhibitor concentration log C for mild steel in 1 M HCl containing acid extract of *Croton sparciflorus* for 6 h at room temperature and higher temperature. Straight lines obtained suggest that the inhibitor follows the Temkin adsorption isotherm.

TABLE-1
CORROSION RATE AND INHIBITION EFFICIENCY FOR MILD STEEL IN 1 M HCl IN PRESENCE AND ABSENCE OF *Croton sparciflorus* EXTRACT AT 298 K FOR 6 h

Concentration (%)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Blank	0.083280	–
0.05	0.005175	93.67
0.1	0.004823	94.10
0.2	0.003017	96.31
0.3	0.002338	97.14
0.5	0.001112	97.64
0.7	0.000719	99.12
0.9	0.002260	97.29

TABLE-2
CORROSION RATE AND INHIBITION EFFICIENCY OF *Croton sparciflorus* EXTRACT AT 323K OBTAINED BY WEIGHT LOSS METHOD FOR 0.5 h

Concentration (%)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Blank	0.08500	–
0.05	0.01512	82.21
0.1	0.01246	85.34
0.2	0.01063	87.50
0.3	0.00757	91.10
0.5	0.00572	93.27
0.7	0.00375	95.59

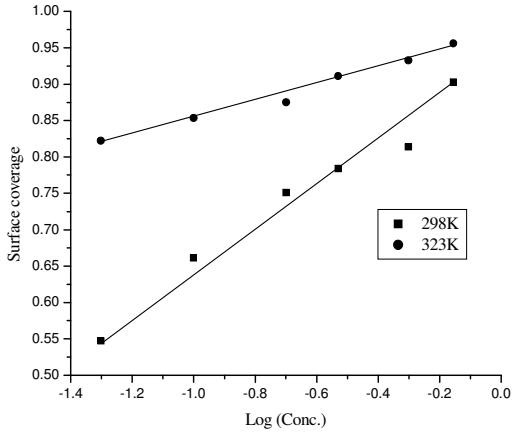

Fig. 1. Temkin adsorption isotherm plot for the different concentration of Ai extract on the mild steel in 1 M HCl at 298 and 323 K

Tafel polarization studies: Fig. 2 shows the Tafel polarization curves. The results obtained by Tafel polarization studies are given in Table-3. The table comprises of the electrochemical parameters such as I_{corr}, E_{corr}, Tafel constants ba and -bc and percentage of inhibition efficiency (IE %). It is evident that the extract brings about considerable polarization of the cathode as well as anode. It was, therefore, inferred that the inhibitive action is of mixed type. The corrosion currents I_{corr} were found to decrease with increasing concentration of the inhibitor.

Electrochemical impedance measurements: The Nyquist representation of the impedance behaviour of mild steel in 1 M HCl with and without the extract is shown in Fig. 3. The impedance diagram gave semi-circle type appearance, indicating that the corrosion of mild steel is mainly controlled by charge transfer process[7]. Table-4 shows the charge transfer resistance (Rct), double layer capacitance (Cdl) and percentage of inhibition efficiency (IE %). Rct values were calculated from the difference in impedance at lower and higher frequencies. To obtain the double layer capacitance (Cdl), the frequency at which the imaginary component of the impedance is maximal (Z" max) was found to be represented as:

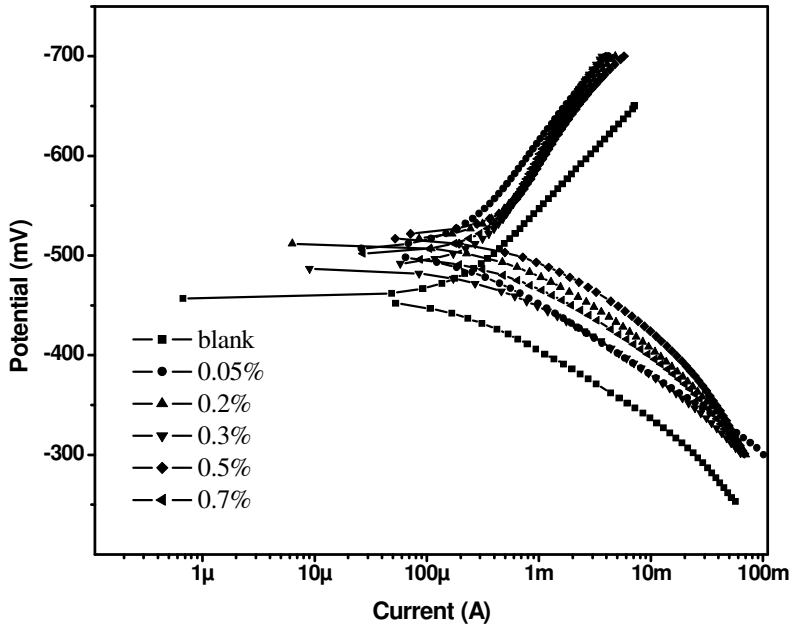

Fig. 2. Potentiodynamic polarization curves for mild steel in 1 M HCl in the absence and presence of different concentration of *Croton spaciflorus* extract

TABLE-3
ELECTROCHEMICAL POLARIZATION (TAFEL) PARAMETERS FOR THE CORROSION OF MILD STEEL IN 1M HCl CONTAINING WITH AND WITHOUT *Croton spaciflorus* EXTRACT

Conc. (%)	$-E_{corr}$ (mV)	I_{corr} (mA/cm^2)	b_a (mV/dec)	$-b_c$ (mV/dec)	R_p (Ωcm^2)	R_p IE (%)	I_{corr} IE (%)
Blank	488	1.075	59.5	158	17.74	–	–
0.05	484	0.480	58.2	155	30.28	53.63	55.35
0.20	483	0.300	59.0	153	61.63	73.20	72.09
0.30	480	0.250	59.5	158	75.07	76.36	76.74
0.50	463	0.175	58.3	153	104.74	83.05	83.72
0.70	460	0.150	56.7	150	119.11	85.10	86.05

TABLE-4
ELECTROCHEMICAL IMPEDANCE PARAMETERS FOR MILD STEEL IN 1 M HCl CONTAINING DIFFERENT CONCENTRATION OF *Croton spaciflorus* EXTRACT

Conc. (%)	Rct (Ωcm^2)	Cdl (μFcm^2)	IE (%)
Blank	30.33	850	–
0.05	98.68	386	54.51
0.20	110.30	242	72.50
0.30	145.90	177	79.21
0.50	188.60	172	79.78
0.70	211.00	113	85.63

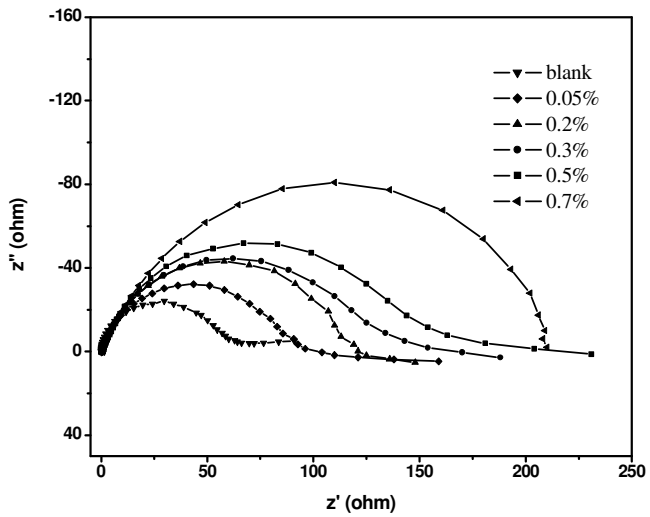

Fig. 3. Impedance diagram for mild steel in 1 M HCl in the presence and absence of different concentration of *Croton spaciflorus* extract

$$Cdl = \frac{1}{2\pi Z'' \max Rct}$$

it is found that Rct values increased with increasing inhibitor concentration.

Mechanism of inhibition: The results obtained indicate that the *Croton sparciflorus* extract performs a good inhibition for the mild steel in acidic medium at room temperature as well as higher temperatures. A chemical analysis of plant extract by FTIR spectrum for HCl extract is shown in the Fig. 4. It shows the absorption peaks at 3439 and 1637 cm^{-1} corresponding to the absorption due to OH and C=O functional groups, while absorption at 1540 and 1456 cm^{-1} corresponds to the extended conjugated benzenoid system. The weak band appears at 1205 cm^{-1} indicates the presence of amine group. On the basis of above mentioned evidence the HCl acid extract may contain the alkaloid and ketonic terpenoids reported by earlier studies.

Conclusion

(**1**) Acid extract of *Croton sparciflorus* was found to be effective in suppressing corrosion in acid medium. (**2**) The inhibition efficiency increases with increase in concentration of the inhibitor and immersion period. (**3**) The high temperature resistance nature of the extract indicates that it can play an important role in water-cooling system. (**4**) The extract obeys Temkin adsorption isotherm. (**5**) From the electrochemical studies it is evident that the extract act through mixed model of inhibition. (**6**) The biodegradable extract of *Croton sparciflorus* leaves were found to be an effective inhibitor and can be safely used without toxic effects and pollution problem. (**7**) Highly cost effective as the plant is freely available at free of cost.

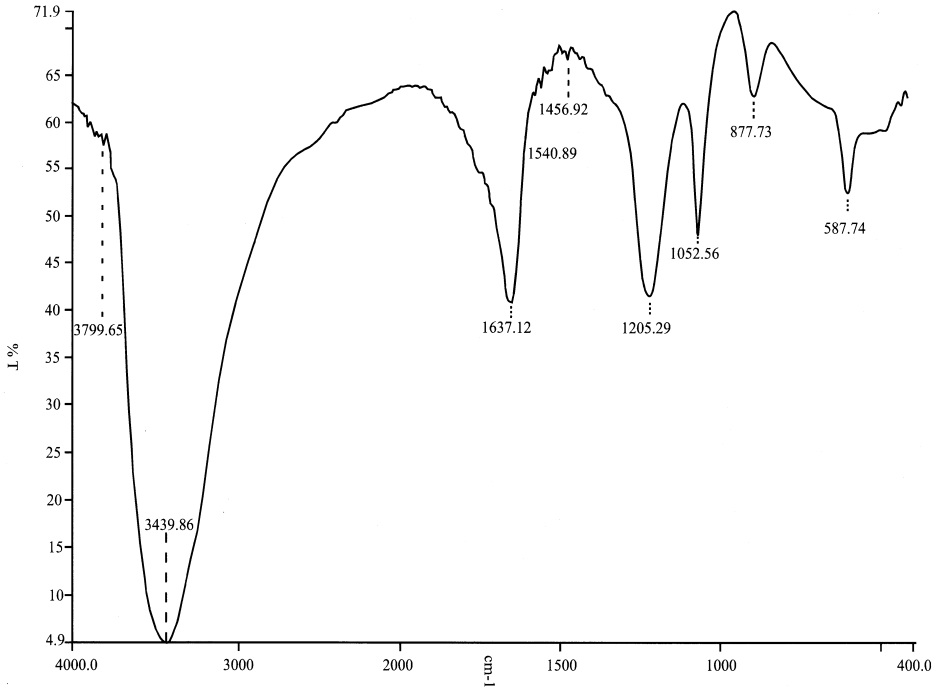

Fig. 4. FTIR spectrum of 1 M HCl extract of *Croton sparciflorus*

ACKNOWLEDGEMENTS

One of the authors (P.K. Kasthuri) expresses his sincere thanks to Dr. L.P. Thangavelu, the Chairman, Dr.Senthilkumar, Principal and Mr.S.Gopu, Head of the department of Science and Humanities, PPG Institute of Technology, Saravanampatti, Coimbatore-35, Tamil Nadu, India.

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(*Received*: 17 January 2009; *Accepted*: 9 September 2009) AJC-7849