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Investigation of Corrosion Protection Efficiency of Indigo Carmine on Carbon Steel in Acidic Environment

K. Palanisamy[1], A. Sekar[2,*]

[1]*Srinivasan College of Arts and Science, Perambalur – 621 212, Tamil Nadu, India.*
[2]*Nehru Memorial College, Puthanampatti, Trichy – 621 107, Tamil Nadu, India.*

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ABSTRACT

The corrosion inhibition of indigo carmine in 0.5 M H_2SO_4 on carbon steel was investigated using weight loss and electrochemical methods in room temperature. The corrosion rates of carbon steel decreased with the increasing concentration of indigo carmine. The charge transfer resistance value increased with increase in concentration. The results of EIS and polarization curves demonstrated that film of the inhibitor was able to protect metal surface from corrosion effectively. The inhibition efficiency of indigo carmine decreased with increase in temperature, suggesting a physical adsorption mechanism, which was found to follow Langmuir adsorption isotherms. The obtained results were confirmed by surface examination using scanning electron microscope.

1. Introduction

The usages of metal in industry are increased every year continuously. Corrosion on this metal is a regular phenomenon, in continuous the protecting of this metal corrosion is a taunting process [1-3]. Various techniques were applied to eliminate corrosion such as applying surfactants on the metal surfaces, treatment with chemical compounds etc. [4-5]. Mostly organic compounds are mixed with acidic medium and inhibition ability of selected organic compounds [6-10] was measured in different methods. It was found that organic compounds which have functional groups (hetero atoms) are highly reactive against metal corrosion. Interestingly, organic compounds were found to be more active at the sites of mild steel corrosion in acidic medium [11-14]. Inhibitors are organic compounds getting absorbed at active site of corrosion or make mono/multilayer film or forming an insoluble complex on the metal surfaces and prevent corrosion. Organic compounds from natural plant source were used widely to prevent the metal corrosion [15]. However, many research evident that natural plant materials are not reactive against corrosion up to the mark. To over this the researchers were opted synthetic organic inhibitors to protect corrosion in extreme environment [16]. In this study we made an attempt to see the effect of corrosion of mild steel in 0.5 M H_2SO_4 solution with Indigo carmine. Treatments were kept for various parameters like time period and temperature. Inhibitory effects were measured with IR, polarization impedance, SEM and isotherm models of Langmuir adsorption isotherms.

2. Experimental Methods

2.1 Sample Preparation

The material used for this study was carbon mild steel supplied in the form of rectangle shape, and the composition (weight percentage) 0.026% of S, 0.035% of P, 0.58% of Mn, 0.104% of C and rest Iron. The size of the carbon mild steel is 3.5 × 1.5 × 0.2 cm, were mirror finish polishing with 200-1200 grade emery paper, degreased with acetone, dried and used for the mass loss measurements, FTIR and SEM for surface studies. The dimensions of the specimens is 1 × 1 × 0.2 cm thickness of the electrode wire encapsulated by Araldite paste and the effective exposed surface area 1 cm² was used for electrochemical studies.

*Corresponding Author
Email Address: karupalani106@gmail.com (A. Sekar)

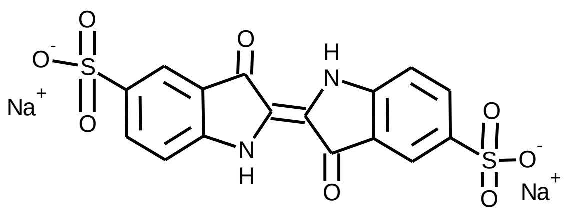

Fig. 1 Structure of indigo carmine

The compound which was used as an inhibitor in this study Indigo carmine structure showed in (Fig. 1). The Inhibitor Indigo carmine where purchased from Sigma-Aldrich which was used without any purification. H_2SO_4 and other reagents were analytical grade chemicals. All the solution was prepared using double distilled water.

2.2 Weight-Loss Method

Weight- loss method is splendidness to find out the IE and corrosion rate of the mild steel which was well polished and immersed in 100 mL of acid solution as a blank, and also the 100 mL of acid with various concentration of Indigo carmine. The mild steel is immersed up to three hours. After over the immersion period the metal taken from the medium and washed using water and dried with hot air. Then the metal kept in mortar then weighted in Shimadzu (AUW2200) four digit balances with accuracy of 0.0001. From the before and after weight of the metal IE and corrosion rate were calculated using the following equations.

$$IE = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

$$CR = \frac{87.6 \times \text{weight loss}}{d \times A \times t} \quad (2)$$

2.3 Electrochemical Study

The carbon steel coupons of size 1 cm² were embedded with epoxy and polished with emery sheets (80-1000) washed with double distilled water, sonicated with acetone and finally dried in hot air. The carbon steel,

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saturated calomel electrode and platinum foil were used as working, reference and counter electrodes, respectively. Impedance measurements were carried out in the frequency range of 100 kHz - 0.01 Hz with sinusoidal amplitude of 0.01 V. ZsimpWin 3.22 software was used for data fitting and calculation. Before commencing impedance study, working electrode was immersed for 45 min in test solution to attain steady state potential.

Tafel polarization curves were obtained under potentiodynamic conditions ranging from ±250 mV at open circuit potential and at the scan rate of 0.001 V/s. Tafel slope constants were calculated by extrapolating the Tafel line.

$$IE\ \% = \frac{R_{ct\,(inhi)} - R_{ct\,(blank)}}{R_{ct\,(inhi)}} \times 100 \qquad (3)$$

$$IE\ \% = \frac{i_{corr\,(blank)} - i_{corr\,(inhi)}}{i_{corr\,(blank)}} \times 100 \qquad (4)$$

3. Results and Discussion

3.1 Weight Loss Method

The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability [17]. The values of inhibition efficiency and corrosion rate obtained from weight loss method at different concentrations of indigo carmine at 303 K are summarized in Table 1. These results show that the indigo carmine inhibits the corrosion of carbon steel in 0.5 M H_2SO_4solution, and the corrosion rate decreases gradually with increasing inhibitor concentration at 303 K. The corrosion rate was found to depend on the concentration of the indigo carmine and inhibition efficiency increases with concentration increasing, the maximum inhibition of 92.4% is achieved at 250 ppm. From the Table 1, it is clear the inhibition efficiency increases with inhibitor concentration. Maximum the inhibition efficiency, lesser will be corrosion rate. The corrosion rate decrease from In other words, the addition of the molecules to 0.5 M H_2SO_4solution retards carbon steel corrosion, and the extend of retardation is concentration dependent.

Table 1 Corrosion rate and the inhibition efficiency obtained by mass loss method for carbon steel immersed in 0.5 M H_2SO_4 in the absence and presence of indigo carmine

Indigocarmine (ppm)	W_0 (mg)	W_1 (mg)	Weight loss (mg)	Average weight loss (mg)	IE %	CR x 10^3
Blank	7.3526	6.8954	0.4572	0.4839	-	-
	8.278	7.7674	0.5106			
50	7.4565	7.2043	0.2522	0.2534	47.63	173
	7.3386	7.0839	0.2547			
100	7.5163	7.3361	0.1802	0.1701	64.84	116
	7.559	7.399	0.16			
150	7.1927	7.1415	0.0512	0.0559	88.44	382
	7.4234	7.3627	0.0607			
200	7.5139	7.4701	0.0438	0.0429	91.13	293
	7.702	7.66	0.042			
250	7.1217	7.0783	0.0434	0.0366	92.42	250
	7.4437	7.4138	0.0299			

3.2 Electrochemical Impedance Spectroscopy

The Nyquist diagrams obtained with and without indigo carmine were illustrated in Fig. 2. Addition of indigo carmine in 0.5 M H_2SO_4 acid solution increases the charge resistance (R_{ct}) and decreases the double layer capacitance (C_{dl}) which can be attributed to adsorption of inhibitor molecule on the surface and hydrophobic nature of the inhibitor [18]. The diameter of the semi-circle increases as the concentration of indigo carmine increases. The depression in semicircle loop is usually attributed to the roughness and other in homogeneity's of the solid electrode [19]. The increased R_{ct} values with increasing the concentration of the inhibitors correspond to enhanced impedance to electrochemical corrosion at high inhibitor concentration. The constant phase element (CPE) factor has been substituted for capacitance to fit the Nyquist circle.

$$Z_{CPE} = [Y_0(2\pi f_{max})^n]^{-1} \qquad (5)$$

Where Y_o is the admittance value of the capacitance, f_{max} is the maximum frequency of the imaginary line and n is the phase shift. If n is a 0, -1, 1, and then CPE value represent pure resistor, inductor and capacitor, respectively. Circuit used in the fitting is showed in Fig. 3. The data obtained from above mentioned equivalent circuit are presented in Table 1. The data show that value of R_{ct} increased from 4.9 Ωcm^2 for the blank to 143.5 Ωcm^2 with addition of 250 ppm of indigo carmine [20]. The increase in R_{ct} values is attributed to the formation of an insulating protective film at the metal/solution interface. The decrease in C_{dl} values can be attributed due to decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, which suggests that the studied indigo carmine inhibit mild steel corrosion by adsorption at the metal/solution interface, thereby reducing the surface contact between the mild steel and aggressive solution Hetero atoms like nitrogen and oxygen in indigo carmine facilitate adsorption on the surface and forms protective layer, which acts as a barrier from environment.

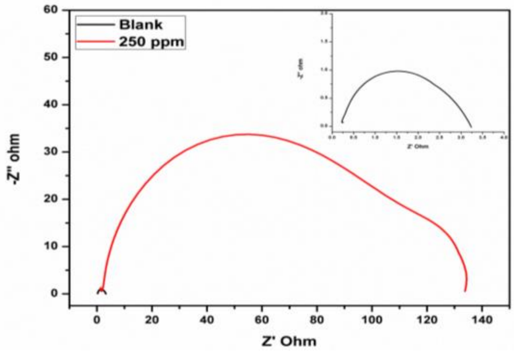

Fig. 2 Nyquist plots of carbon steel in the absence and presence of 250 ppm of indigo carmine

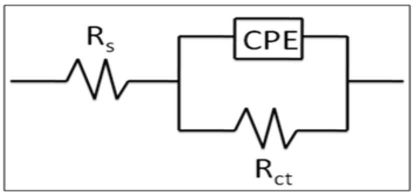

Fig. 3 Equivalent circuit diagram

Table 2 The electrochemical impedance parameters of carbon steel in the absence and presence of 250 ppm of indigo carmine

Indigo carmine(ppm)	R_s ohm	N	C_{dl} (µF/cm²)	R_{ct} (Ω cm²)	IE %
Blank	0.19	0.7	1512	2.8	-
250	0.14	0.7	40	124.7	97.7

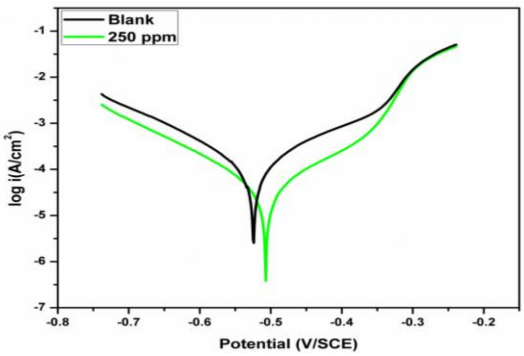

Fig. 4 Polarization curve of carbon steel in the absence and presence of 250 ppm of indigo carmine

3.3 Potentiodynamic Polarization Study

Tafel plots are used to analyze the anticorrosion properties of the inhibited sample [21]. Fig. 4 shows the Tafel slopes of carbon steel in the absence and presence of the indigo carmine in 0.5 M H_2SO_4. From this experiment, corrosion parameters such as i_{corr} anodic slope (β_a), cathodic slope (β_c) and E_{corr} were calculated and are tabulated in Table 3. It is clear from the Table value that the i_{corr} value decreased from 1.477 to 0.4 × 10^{-4} A, which is attributes to the passivation effect indigocarmine, hindered the corrosive ion like SO_4^{2-} from the penetration. The inhibition efficiency (IE) of the indigo carmine was 70.3%, indicating that the 250 ppm was better than blank. Hence, 250 ppm is the optimum concentration with higher corrosion protection efficiency. On observing the (Fig. 2) it can be understood that anodic and cathodic current were diminished comparing to blank Tafel plots by introducing indigocarmine in acid medium. Indigo carmine acted as mixed inhibitor in acidic medium, because it didn't exceed ± 80 mV with respect to the open circuit potential. Both the anodic and cathodic curve current have been decreased considerably, relates to the blocking of anodic and cathodic area for the metal dissolution and reduction of hydrogen gas, respectively.

Table 3 Polarization parameters of carbon steel in the absence and presence of 250 ppm of indigo carmine

Indigo carmine (ppm)	$-E_{corr}$ (V)	i_{corr} ($\times10^{-4}$A)	β_a 1/V	β_c 1/V	R_p (Ω.cm^2)	IE (%)
Blank	524	1.477	6.7	7.0	215	-
250	506	0.4375	7.8	8.2	619	70.3

3.4 Temperature Effect

The effect of temperature on carbon steel in the absence and inhibited solutions of 0.5 M H_2SO_4 was studied at temperature range of 30-70 °C (Fig. 5). Acid solutions were inhibited by adding optimum concentrations of indigo carmine. The obtained corrosion inhibition efficiency is shows when temperature increases, in the absence and presence of inhibitor, the corrosion rate increases. Accordingly, the efficiencies of indigo carmine were temperature dependent. The fact that corrosion rate was increased with increasing temperature. Increasing corrosion rate with temperature increasing may be due to the change in the nature of the adsorption mode. Physical adsorption was evident at lower temperatures, whereas chemisorption was favored at higher temperatures.

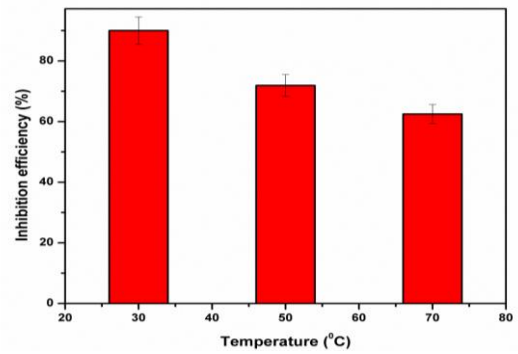

Fig. 5 Effect of temperature on carbon steel at various temperature in the presence of 250 ppm of indigo carmine

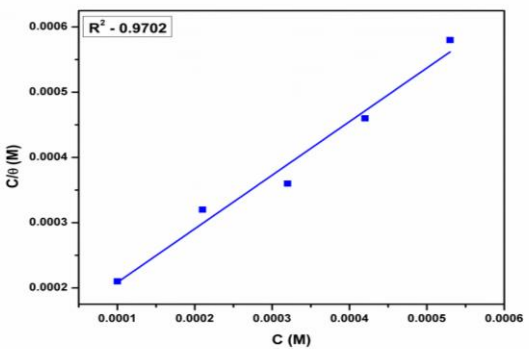

Fig. 6 Langmuir adsorption isotherms of different concentration of indigocarmine in 0.5 M H_2SO_4 medium on carbon steel

3.5 Adsorption Isotherm

The adsorption process of the inhibitors is greatly influenced by structure, charge distribution and nature of the metal. Langmuir adsorption is obeyed by increasing of surface coverage due to enhanced inhibitor concentration and obtains the maximum coverage. Many attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Freundluich and Frumkin. The best fit is obtained with the Langmuir isotherm (Fig. 6) [22]. In the scrutinizing of inhibition mechanism of an inhibitor, thermodynamic properties are very important. The adsorption equilibrium relation is given in the following equation

$$K_{ads} = \frac{\theta}{(1-\theta)C} \qquad (6)$$

where, K_{ads} is the adsorption equilibrium constant, θ is the surface coverage and C is the concentration of the inhibitor. The plot of C/θ vs C gives a straight line as shown in Fig. 6. The slope of the graph was closed to unity, confirming the Langmuir adsorption isotherm.

Thermodynamic properties of the inhibitor are necessary to relate inhibition mechanism on carbon steel with the adsorption of inhibitor. Free energy of adsorption (ΔG_{ads}) of the inhibitor was calculated using the following relation (3).

Table 6 Equilibrium constant and free energy of adsorption of optimum concentration of indigo carmine at different temperature

Inhibitor	Concentration (ppm)	K_{ads} (mol^{-1})	$-\Delta G_{ads}$ (k J mol^{-1})
indigo carmine	50	24074	35.5
	100	22910	35.4
	150	21698	35.2
	200	8867	33.0
	250	8465	32.9

$$\Delta G_{ads} = -RT\ln(55.5\ K_{ads}) \qquad (7)$$

The negative value of ΔG indicates the stability of the protective film on the metal substrate and spontaneity of the adsorption process. From Table 6, it is clearly seen that free energy of adsorption value becomes less negative with the decrease in K_{ads} which indicates desorption of inhibitor as function of increasing temperature. If the ΔG >-40 kJ/mol, the adsorption of the inhibitor is said to be chemisorption or ΔG <-20 kJ/mol then it will be physisorption [23]. The calculated ΔG value for the inhibitor is around -34 kJ/mol and hence the adsorption of inhibitor in its medium is both by physical and chemical adsorption.

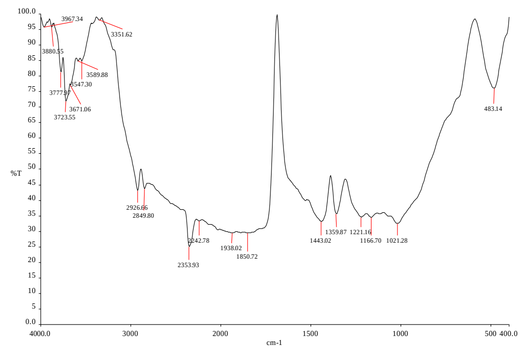

Fig. 7a The FTIR spectrum of mild steel immersed in 0.5 M H_2SO_4 in the absence of indigo carmine

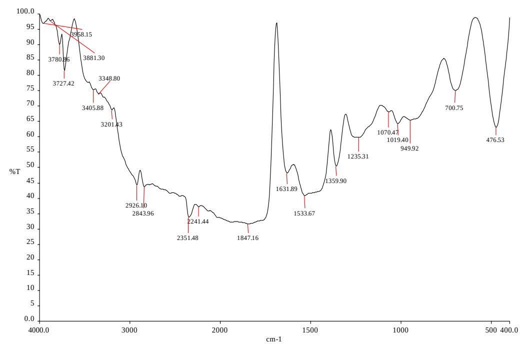

Fig. 7b The FTIR spectrum of mild steel immersed in 0.5 M H_2SO_4 in the presence of indigo carmine

3.6 FTIR Study

The FTIR spectrum of the sample scratched from the metal surface immersed in the absence and presence of the indigo carmine were shown in Fig. 7 (a, b) respectively. The slight differences in the IR spectra are observed in the fingerprint region due to difference in alkyl chain lengths. The IR bands at 700 cm^{-1} are due to C-N stretching vibrations. The observed vibration bands at 1359 cm^{-1} are due to C-C stretching vibrations. The band at 2926 cm^{-1} is due to the aliphatic asymmetric C-H stretching vibrations. Features above 3000 cm^{-1} were from the C-H vibrational modes of the imidazolium ring, where the broad band between 3201 and 3405 cm^{-1} peaks is common to the indigo carmine after mild steel immersion and it is due to the formation of indigo carmine/Fe complex in solution.

3.7 Scanning Electrochemical Microscope (SEM) Study

SEM image of the carbon steel in 0.5 M H_2SO_4acid medium for 3 h in the absence and presence of indigo carmine are shown in Figs. 8a and b shows the grooves on the metal surface, due to the grinding. It can be viewed that the sample surface totally ruptured in the absence of inhibitor (Fig. 8b). Conversely, Fig. 8c shows considerable protecting ability of the indigo carmine to corrosion on carbon steel, it is totally attributed to the good adhesion property on the specimen surface.

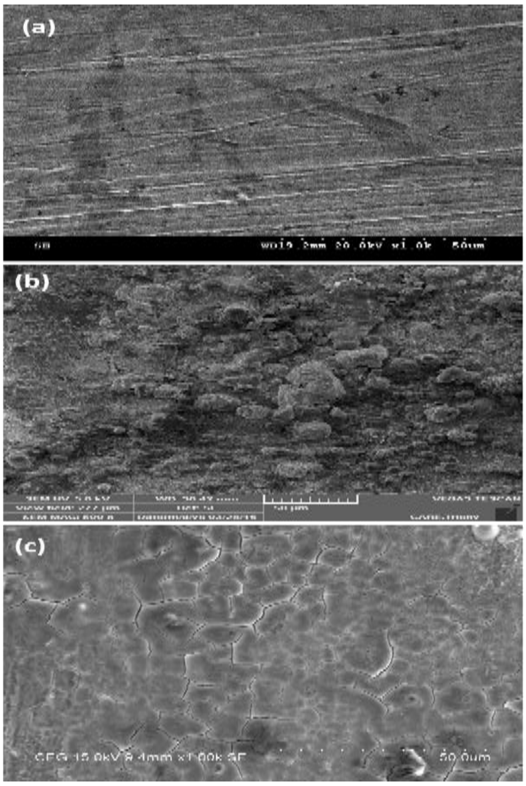

Fig. 8 SEM image of (a) Bare metal (b) Metal immersed in 0.5 M H_2SO_4 (c) metal immersed in 250 ppm of indigo carmine in 0.5 M H_2SO_4

4. Conclusion

Indigo carmine was found to be an effective inhibitor for the corrosion of carbon steel in 0.5 M H_2SO_4. Gravimetric measurements revealed that inhibition efficiency reached 97% at a concentration of 250 ppm. Potentiodynamic polarization parameters reveal that the indigo carmine affects both anodic and cathodic reactions and acts more or less as a mixed inhibitor. The inhibition is due to the adsorption of inhibitor on the surface of the metal, thereby blocking the active sites. Inhibition efficiency calculated from impedance and polarization were in good agreement. Furthermore, Inhibition efficiency increased with extract concentration but decreased with temperature, suggesting physical adsorption. Adsorption of indigo carmine was found to follow Langmuir isotherm model. Morphological studies inferred the formation of a protective layer over the carbon steel surface.

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