Refined Cleansing Characteristics of HCL with Trihydroxy Chalcone in Mild Steel

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Abstract— **Evaluated the corrosion inhibition efficiency of trihydroxychalcone (THC) on mild steel (MS) in hydrochloric acid medium and studied the influence of temperature and concentration of THC on the inhibition efficiency. Experimental weight loss data reveals that at high temperature the inhibition efficiency is suppressed which may be due to depletion of adsorbed THC from the specimen MS surface., This is supported by the thermodynamic parameters such as heat of adsorption (*Q*), change in entropy (Δ*S*), change in free energy of (Δ*G*), corrosion rate (*CR*), energy of activation (*Ea*) are derived from experimentally measured weight loss of the specimen MS plate.**

Keywords- Trihydroxychalcone, corrosion, mild steel.

I. INTRODUCTION

Metals and their alloys have a lot of applications in our day- to-day live. But metals are unstable and inclined to react with their environments to form chemical compound of lower energy in a more stable state, which is named as corrosion. This has led to many industrial problem that has attracted a lot of investigations in recent years [1]. Mild steel is an industrially important alloy of carbon, which is widely used in petrochemical, automobile, metallurgical and many more industries.

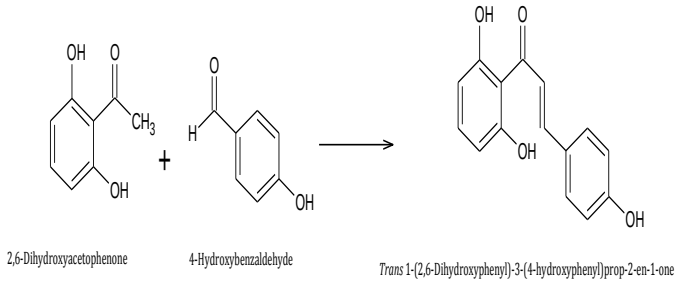
Petrochemical, chemical and metallurgical industries use HCl in various applications more particularly as cleansing agent. Acid pickling is one of the most widely used methods for effective cleaning of mild steel in several industries, but initiates corrosion in mild steel [2-4]. Hence it is obligatory to protect the alloys from dissolution. Out of several methods, addition of corrosion inhibitors in small quantities is proved to be a simple and effective method for the prevention of corrosion, especially in acidic medium.

Chalcones are compounds with various substitutions on the two aromatic rings of 1.3-diphenyl-2-prpoene-1-one. They are considered as the originator of flavonoids and isoflavonoids which are rich in edible plants. But from plants stable chalcones moiety cannot be isolated, because of the presence of enzyme synthetase which immediately converts chalcones into flavanones [5]. They exhibit antimalarial [6] antibacterial [7] anticancer [8] antitrichomonal [9] anti-inflammatory [10] and antileishmania [11] activities. Hence they are considered to be eco-friendly compounds.

The use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions [12]. But the present and future needs a nontoxic compound that can protect metals against corrosion without causing environmental problems. Considering the eco-friendly nature of the chalcones, they are studied for anticorrosion properties of mild steel in acid medium [13].

II. . EXPERIMENTAL

A. Synthesis of trihydroxychalcone (1-(2,6dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one); inhibitor compound has been synthesized in the laboratory by the method (Jayapal et al., 2010).



2,6-Dihydroxyacetophenone 4-Hydroxybenzaldehyde *Trans* 1-(2,6-Dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one

The mild steel sheets available in the market has the percentage composition of C=0.32, Mn=0.667, Si=0.234, P=0.035, S=0.025, Cr=0.015, Ni=0.002, Mo=0.008 and balance is Fe. MS Specimen of size 4×2×0.2 cm was polished with different grades of emery papers, degreased with acetone, washed with double distilled water, dried and used [14].

For experiment, pure HCl (merck-61752605031730) and double distilled water were used. 1M HCl solution prepared with double distilled water was used as corrosive environment. The concentrations of inhibitors used are 20, 40, 60, 80 and 100 ppm. The % inhibition efficiency (IE) for various concentrations of the inhibitor was estimated by weight loss method [15]. Thermodynamic parameters such as heat of adsorption of the inhibitor on the metal surface (Q), corrosion rate (CR), change in free energy (ΔG) were also calculated.

FTIR spectra were recorded for the inhibitor and the adsorption product formed between finely powered MS specimen and 100 ppm inhibitor test solution using FITR model Jasco / Japan with spectral range from 400 cm^{-1} to 4000 cm^{-1}.Values of surface coverage (Θ) corresponding to different temperatures are used to obtained best adsorption isotherm. Temkin adsorption isotherm could be applied to investigate the mechanism.The electrochemical measurement were carried out using multichannel potentiostat-Biologic SA with a conventional three electrode set up comprising a platinum counter electrode, a reference calomel electrode (SCE) and a MS specimen as working electrode ($1cm^2$) and the equivalent circuit is given in figure 6. The polarization curves were recorded at the scan rate of 10mV/s for a potential range of -1.4 to 0.6 mV.

Impedance measurements were carried out in the frequency range of 10 KHz to 10 mHz with three electrode set up. The impedance diagrams are given as Nyquist plots. Scanning electron Microscope (SEM) Carl ZEISS-Smart SEM, EVO18-special edition (EVol.8.15.66) (MA&LS Series) was used. Scanning was done with voltage 20KV and filament current 1.98A. Photographs were recorded for polished mild steel specimen exposed to 1M HCl corrosive environment and specimen immersed in 250ppm test solution.

III. RESULT AND DISCUSSION

3.1 Weight loss studies

The influence of temperature on percentage inhibition efficiency was studied by conducting weight loss measurement from 303K to 333K, containing different concentration of the inhibitor (Table 1). It shows that IE increases linearly with increasing in inhibitor concentration (Figure 1). IE also increases with increasing temperature of the corrosion medium from 303K to 323 K and then decreases further with rise in temperature. The increased IE up to 323 K is highly significant as many applications will be done around these temperatures. It is reported that the analog of the inhibitor forms a complex with iron and thus adhere as a thin film on the metal surface. The inhibitor exits in the quinone tautomer rather than ketone form. The inhibitor provides increased efficiency as the temperature is increased up to 323K reflecting the increased adsorption of the compound. Above 323 K, the inhibitor desorbs and dissolves them in the corrosive medium thus decreasing the IE [16]

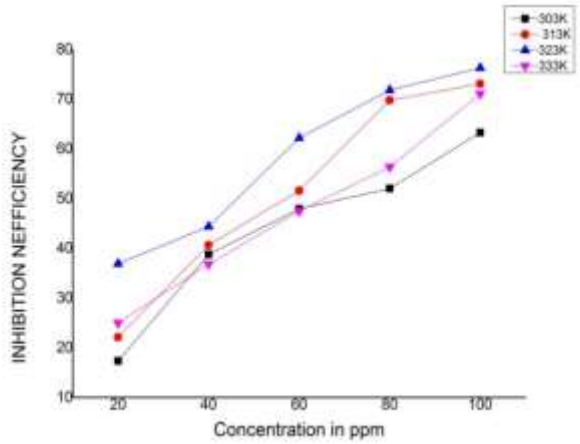


Figure 1. Efect of temperature and concentration on Inhibition effecienc

Table 1. IE of 1-(2,6-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2- en-1-one on mild steel in acid medium

Conc. Of the inhibitor (ppm)	Weight loss. G				Inhibition efficiency %			
	303K	313K	323K	333K	303K	313K	323K	333K
0	0.0098	0.0903	0.0894	0.2261	..	..	..	..
20	0.0081	0.0703	0.0564	0.1695	17.35	22.15	36.91	25.03
40	0.006	0.0536	0.0497	0.1428	38.78	40.64	44.41	36.84
60	0.0051	0.0437	0.0338	0.1187	47.96	51.61	62.19	47.50
80	0.0047	0.0273	0.0252	0.0986	52.04	69.77	71.81	56.39
100	0.0036	0.0243	0.0212	0.0654	63.27	73.09	76.29	71.07

3.2 Thermodynamics of inhibition

The free energy change (Δ G) for the adsorption was calculated using the formula

The heat of adsorption of the inhibitor on MS plate is calculated by

$Q_{ads} = 2.303R\ [\log(\Theta_2/1-\Theta_2)-\log(\Theta_1/1-\Theta_1)\ x\ T_2T_1/T_2.T_1]$.

The positive Q_{ads} values (Table 2) indicate that IE increases with rise in inhibitor concentration (Ekpe *et al*., 1995). But for temperature above 323K, the value decreases, which is reflected in the IE values.

The corrosion rate (CR) was calculated in mmpy using the formula,

CR = 87.6 x W/DAT,

where 'W' is the weight loss in mg, 'D' is the density of mild steel, 'A' is the area of exposure in $(cm)^2$ and 'T' is the time in hours [17]. Even at lowest concentration, the inhibitor is able to bring down the corrosion rate substantially Corrosion rate decreases from the blank value and the maximum decrease is obtained for 250 ppm inhibitor concentration.

Table 2. Free energy change and heat of adsorption of the inhibitor on the metal surface

	303K	313K	323 K	333 K	Heat of adsorption, Q (KJ/mol)		
Conc. of the inhibitor (ppm)	Δ G (KJ/mol)	ΔG (KJ/mol)	ΔG (KJ/mol)	ΔG (KJ/mol)	303-313	313-323	323-333
0	-	-	-	-	-	-	-
20	-30.017	-30.78	-32.60	-31.19	23.98994	56.86662	-44.2331
40	-31.053	-31.25	-31.64	-30.85	6.150244	12.15431	-24.7901
60	-30.98	-31.344	-32.44	-30.93	11.50857	34.18489	-47.1415
80	-30.66	-32.564	-32.81	-31.11	59.50792	7.800468	-53.4784
100	-31.27	-32.41	-32.84	-32.16	35.92722	13.3488	-21.2479

3.3 FTIR analysis of inhibitor

IR spectra were recorded for the synthesized inhibitor and the adsorption product between the inhibitor and the MS powder. On comparing the spectra, O-H stretching frequency has shifted from 3215.6 to 3403 cm^{-1}. The carbonyl group frequency has shifted from 2665 to 211637 cm^{-1}. The carbon -carbon double bond has also shifted from 1512 to 1637 cm^{-1}. (Figure 2; Figure 3) These changes in group frequency reveal the interaction of functional groups present in the inhibitor with mild steel is responsible for adsorption thus preventing corrosion. Aromatic adsorption frequency has also undergone changes due to interaction with mild steel.

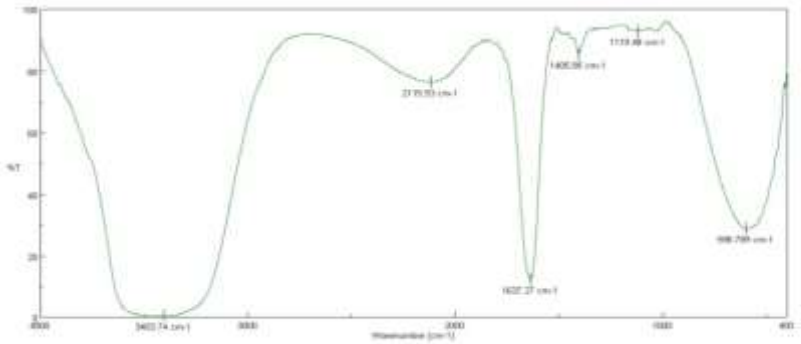


Figure 2. FTIR spectrum of (1-(2,6-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2- en-1-one) recorded in KBr, 400 cm^{-1} to 4000 cm^{-1}

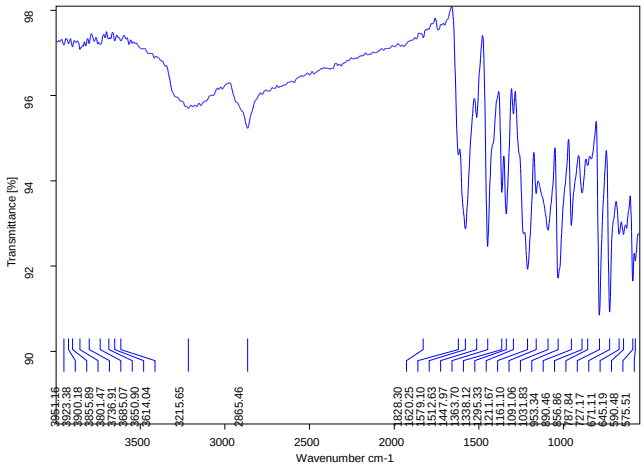


Figure 3. FTIR spectrum of the inhibitor and MSpowder

3.4 Adsorption isotherm

According to Temkin's adsorption isotherm,

$C^{a\Theta}=KC$

Where Θ is surface coverage, C is Concentration of the test solution K is the equilibrium constant of adsorption and 'a' is the molecular constant.

The surface coverage area when plotted against "log C" showed a line plot suggesting Temkin adsorption isotherm. The inhibition was based on the coverage of the metal surface by the inhibitor molecules thus preventing the contact of the corroded species with acid. Temkin adsorption isotherm reveals that IE increases with increase in concentration of the inhibitor (Figure 4).

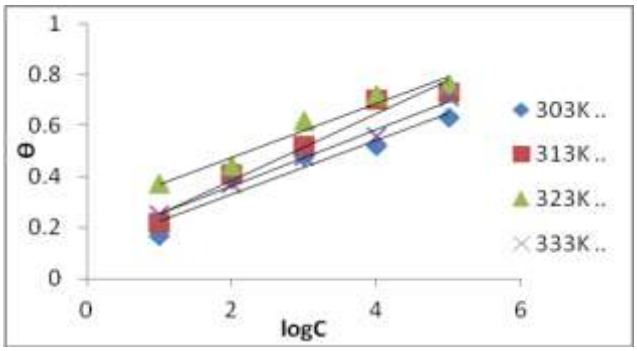


Figure 4. Temkin adsorption isotherm recorded at temperatures from 303 K to 333 K

3.5 Electrochemical Impedance studies

The impedance Nyquist plot is depicted in Figure 5 and the derived parameters are given in Table 3. The plot shows a depressed capacitive loop which arises from the time constant of the electrical double layer and charge transfer resistance. The impedance increases with increase in the inhibitor concentration and subsequently the inhibition efficiency is increased. A depressed semicircle is attributed to frequency dispersion which arises because of different physical characteristics such as roughness and in-homogeneity of the solid surfaces, impurities, grain boundaries and distribution of the surface active sites [18].

The charge transfer resistance (Rp) values increase in the presence of the inhibitor though not showing a regular increase. The double layer capacitance (Cdl) value decreases with increase in concentration of the inhibitor and the diameter of the semicircles increases with increase in concentration of the inhibitor. This is due to the adsorption of the heteroatom of the inhibitor on the metal surface [19] which is also confirmed by FTIR analysis. The increase in resistance towards charge transfer reaction viz., corrosion reaction with increase in inhibitor concentration is shown by the increased R_P values.

Table 3.ectrochemical parameters of corrosion in acid medium with and without inhibitor

Conc.(ppm)	E_{Corr} -mV	C_{corr} µA	β_a mV	β_b mV	C_{dl} (μFcm^{-2})	R_p (ohm/cm)	%IE
blank	474.43	916.39	121.1	170.2	107	38.6	-
20	458.90	586.02	108.6	191.4	63.43	58.35	36.05
40	466.73	567.91	115.4	246.00	135	43.96	38.02
60	477.35	492.81	121.6	193.3	93.13	65.37	46.22
80	469.25	444.16	122.6	240.8	115.13	34.69	51.53
100	476.07	431.48	127.7	174.9	73.13	81.77	52.91

3.6 Electrochemical Tafel Polarization analysis

The electrochemical parameters are given in Table 5. The obtained E_{corr} values reveal that, it is a mixed mode of inhibition, as the E_{corr} values of the blank and the solutions with different concentration of the inhibitor, do not vary much [20]. The mixed mode of inhibition is again proved by β_a and β_c values as they do not increase or decrease in a regular manner. The potentiodynamic curves are shown in Figure 6. The inhibition efficiency is calculated using the formula

$$\% IE = [(I_{corr} - I'_{Corr)} / I_{corr}] X 100$$

Where, I_{corr} is corrosion current of blank, I'_{corr} is corrosion current of solution in the presence of inhibitor [21]. The inhibition efficiency obtained from weight loss and electrochemical measurements are in good agreement at all concentrations.

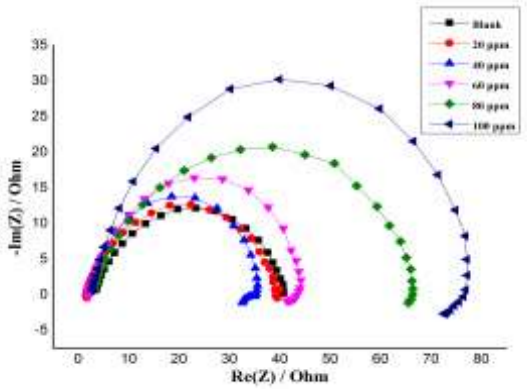


Figure 5. Electrochemical impedance spectrum recorded at Inhibitor concentration range 20ppmto 100 ppm

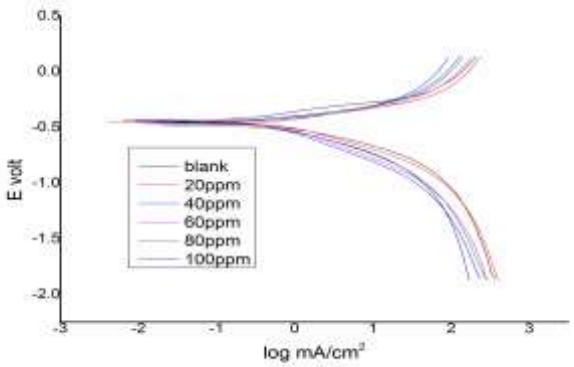
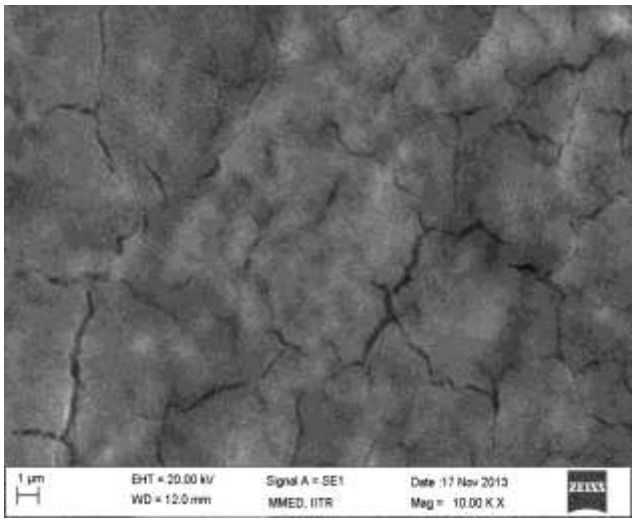
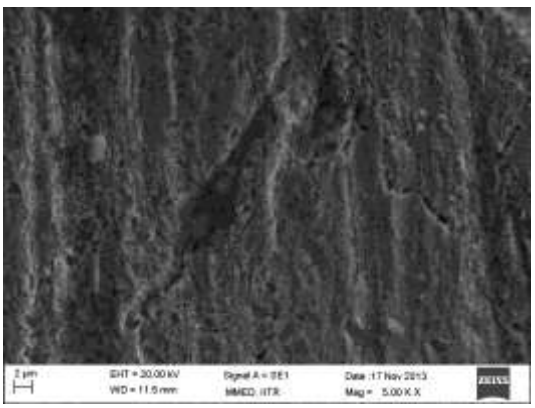


Figure 6. Tafel polarization curves recorded at various Inhibitor concentrations

3.7 SEM Studies

The surface morphology of mild steel is studied with and without inhibitor in hydrochloric acid medium using scanning electron microscope (SEM). The SEM photograph of mild surface is clear from any pits or protrusion while the photograph of acid immersed MS plate shows cracks, pits and blisters of severe category. However, the specimen in the presence of inhibitor is far better than others in acid medium alone. This reflects the effect of inhibitor in protecting the MS specimens.





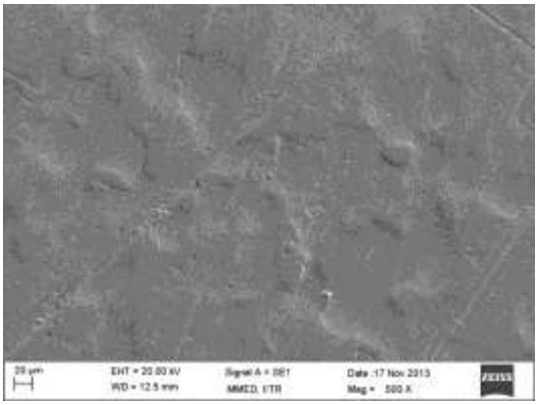


Figure 7. SEM images of a. Specimen in 1M HCl, b. polished specimen c. specimen immersed in 100ppm inhibitor solution

4. CONCLUSION

The inhibitor studied has increased IE up to 323K, but decreases above the said temperature, which is highly significant as this substance can be used at relatively higher temperature for certain applications. This is further substantiated by thermodynamic studies, which also suggest that the inhibition is spontaneous. IR, impedance and SEM studies vindicate the interaction between metal surface and inhibitor reflecting corrosion protection. Electrochemical parameters show that the mode of inhibition is mixed type.

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