

P.Kannan^a, P.Jithinraj^b, M.Natesan^{*}

^a St. Joseph's College, Trichy 620002, Tamil Nadu, India. ^b Calicut University, Kerala India. ^{*} Central Electrochemical Research Institute, Karaikudi 630006. India

ABSTRACT

Four synthetic organic compounds and one complex compound were developed as volatile corrosion inhibitor for hydrogen sulphide environment of mild steel. Four compounds such as OTP, OTS, OTC, OTB and one complex compound DCHAB were synthesized as VCI's. Electrochemical impedance spectroscopy of volatile corrosion inhibitor monitor (VCIM) was applied to studied the effect of the above five inhibitor on the corrosion inhibitor of mild steel in this electrolyte layer. DCHB shows the best protective inhibition efficiency compared with other remaining inhibitors. And its adsorption of DCHB shows by the EIS, LPR, and FTIR. All the shows that one DCHAB molecule has three nitrogen atom to coordinate with one Fe atom. It will be used as a remedy for the inner pipe line corrosion, which was exploited for the transportation of natural gases.

KEY WORDS

Mild Steel, Volatile Corrosion Inhibitor, Inhibition Efficiency, Relative Humidity, Hydrogen Sulphide.

1. INTRODUCTION

The metal is easily suffered from atmospheric corrosion due to the variation of temperature and humidity during transport and storage. If we observe the development of the corrosion inhibitor from the former time, is started approximately at end of II world war. When the VCI present as vapours function by getting adsorbed on to the metal surface and thus forming a

This is observed especially in iron and steel making them passive. This layer separates the metal from the environment. Thus frequent condensation and deposition of vapours thicken this layer. The inhibition is transmitted as vapours, and the vapour phase is controlled by the structure of the crystal lattice and the character of atomic bond in the molecule. The protective vapours expand within the enclosed space until the equilibrium determined by their practical pressure of the vapor is reached [2]. It's known that the application of volatile corrosion inhibitor (VCI) is one of the most practical methods for protection of metal against atmospheric corrosion [3-6]. Generally, the VCI's are a compound raw or synthesized could be used as inhibitor in protection. Amine (nitrogen containing) compounds were used as volatile corrosion inhibitor for atmospheric corrosion [7]. And sodium, potassium were used in the field of corrosion [8, 9]. Ammonium nitrite, urea and amides would have been used as volatile corrosion inhibitor [10-12]. Nitrogen containing bases act as volatile corrosion inhibitor in the sulphur environment [13]. The advantage of the VCI is that the vaporized inhibitor molecule. Steel equipment and pipe line can be efficiently protected from corrosion attacks crude gas by using volatile corrosion inhibitor (VCI) [14-15]. However, some sodium salts of benzoic acid had used as vapour phase inhibitor [16]. If the vapour pressure of the volatile corrosion inhibitor is high, greater will be the adsorption on metal. In practical application less volatile inhibitor is preferable. It will be a long lost protection [17]. Aromatic compound such as, naphthalene has been a VCI at 250-350 °C in the HCl environment. Bayer synthesised cyclohexylamine and dicyclohexylamine as volatile corrosion inhibitor on iron [18]. As definition of kemlet, the protection of silver in the ammonia could be favoured by amine [19]. Not only the cyclic compound but also straight chain amine like octylamine could be used as volatile corrosion inhibitor. And its characterization had been done by Natesan [20]. Adsorption on iron and the protective effect of some ethanol amines on ferrous

and non-ferrous metals was studied. The effect of the chemical structure of volatile corrosion

inhibitors of this type, on desorption kinetics and protective after effect of adsorption films formed on the metal surface in air was analysed [21]. Benzotriazole was used as VCI on silver in H_2S atmosphere [22]. Some time polymer compound has been used as inhibitor for acid medium. For paradigm, VPMA acts as an effective corrosion inhibitor for steel in 2M sulphuric acid medium. The inhibition efficiencies increase by an increase in concentration of VPMA and decrease in temperature [23]. All over the world transportation of petroleum products are being transport thorough pipe line from one country to another. In this long process there must be chance to occur corrosion inside the pipe line by effluent gas like sulphur and chlorine etc. In our paper work, the volatile corrosion inhibitor of OTP, OTS, OTC, OTB, DCHAB were exploited to reduce the corrosion of carbon steel in the hydrogen sulphide environment of different multiphase system of immersion and partially immersion and without immersion condition.

2. EXPERIMENTAL PROCEDURE

Corrosion tests were done in VCIM at 50^0 C. Before experiment the specimens were polished with grit emery paper, degreased by acetone, washed by distilled water and dried in hot air. Then specimens were weighed, and suspended in the hooks and calculate the inhibition efficiency and corrosion rate in the presence and absence of inhibitor in the H_2S gas medium of three various environment of without immersion, partially immersion, fully immersion with corrosive medium of H_2S .

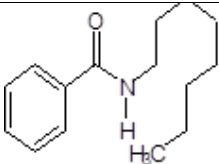
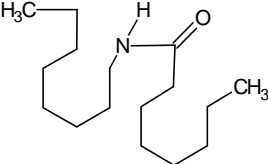
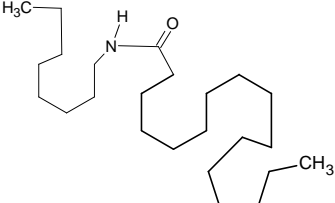
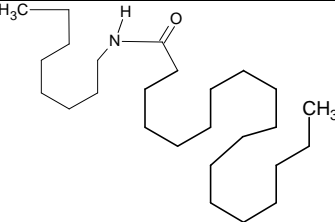
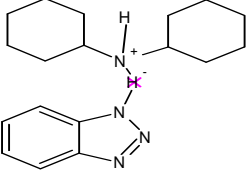
2.1 SYNTHESIS

The synthesis of OTP, OTS, OTC, OTB were prepared by the equimolar mixture of octylamine (Aldrich) with corresponding acids such as palmetic, stearic, caprylic, benzoic acid(Merck) by stirring them at room temperature. And DCHAB was synthesised by

incorporate dicyclohexylamine and benzotriazole (Aldrich). Finally, the synthesized

inhibitor were characterised by FTIR. The molecular structure and weight of the amide inhibitor were shown below the Table.1

Table 1. Structures of VCI's

SL.NO	Structure	Molecular formula & weight	Vapour pressure mmHg	Name of VCI's
1.		C ₁₅ H ₂₃ NO & 233.3492	2.4853×10 ⁻³	OTB
2		C ₁₆ H ₃₃ & 255.4393	2.5653×10 ⁻³	OTC
3		C ₂₄ H ₄₉ NO & 367.652	1.9667×10 ⁻³	OTP
4		C ₂₆ H ₅₃ NO & 395.7051	1.2740×10 ⁻³	OTS
5		C ₁₈ H ₂₉ N ₄ & 301.4498	1.253×10 ⁻³	DCHAB

2.2 MATERIALS AND MEDIUM

The electrolyte solution is prepared by using 0.08M NaCl, 0.01M acetic acid, 0.5 M Na₂S with double distilled water mixed them together and used as electrolyte solution. At the end of the above mixture gives H₂S. The specimens were made from carbon steel with following chemical composition. Carbon-0.07% sulphur- nil, phosphorous-0.008%, silicon – nil, manganese -0.34%, Fe – balance

2.3 GRAVIMETRIC MEASUREMENTS

The Gravimetric test was conducted to evaluate the inhibition effect of the VCI. Specimens of mild steel were made with dimensions of 5 cm x 1 cm x 0.1cm and a hole was drilled in each for suspending purpose. The final geometrical area of each specimen was 10 cm². The test specimens' mill scales were removed by using the pickling solution as given before. Prior to the tests, the metal surface was polished with 1/0, 2/0, 3/0 and 4/0 emery papers, degreased with trichloroethylene, and dried. The specimens were weighed with accuracy of 0.1mg. After initial weighing, the test specimens were exposed in a 1000 ml of glass desiccator with an open weighing bottle containing the solution of inhibitor in Isopropyl alcohol. The specimens were held by hooks in the desiccator over a 500ml of electrolyte solution. This setup was kept in a thermostat water bath maintained at 50°C. This arrangement produced a continuous under saturation of water vapours at 100% relative humidity. The test process included cyclic warming and cooling of the samples in the desiccators of 100% relative humidity. One cycle included a 5 hours exposure in the thermostat. The experiments were carried out in the absence and in the presence of inhibitor. The observations were made at the end of the test period. Specimens were then cleaned using pickling solution. Washed, dried and reweighed. Mass loss was then found to determine the

corrosion rate. The specimens were weighed prior to and after the tests; the corrosion rate was calculated by formula (1), and the inhibition efficiency (IE) by formula (2). The same procedure has been done for the partial and fully immersion of the two different corrosive environments.

$$CR = \frac{W_1 - W_2}{A \times T} \rightarrow (1)$$

$$IE \% = \frac{CR_1 - CR_2}{CR_1} \times 100 \% \rightarrow (2)$$

For EIS technique

$$IE (\%) = \frac{R_{ct} \text{ with (I)} - R_{ct}}{R_{ct} \text{ with (I)}} \times 100 \rightarrow (3)$$

Where,

$R_{ct} \text{ with (I)}$ = Charge transfer resistance with inhibitor.

R_{ct} = Charge transfer resistance without inhibitor

Where CRs is in $\text{g m}^{-2} \text{ h}^{-1}$, A is the specimen area (in m^2), W_1 is initial mass of the specimen, and W_2 is the specimen mass (in g) after the exposure period, T is the exposure period (in hours), and CR_1 and CR_2 are the corrosion rates without and with an inhibitor, respectively. The experiments were carried out in triplicate. i.e. the gravimetric corrosion rate

was listed as an average value for the three specimens studied under identical experimental conditions.

2.4 POTENTIODYNAMIC MEASUREMENT

The linear polarization resistant has been taken with help of two electrode system working and counter electrode mode were consider as a one, and saturated calomel electrode as reference one. The potential value in this paper was referred to SCE. The potentio dynamic measurements were started by changing step wise 60mV/M on a PGP201P potentiostat/galvano static.

2.5 ELECTROCHEMICAL IMPEDENCE SPECTROSCOPY

The cell configuation of EIS was done by the electrochemical measurement unit solartron 1280b. The employed amplitude of $\pm 20\text{mV}$, frequency ranging 0.5Hz to 100 KHz

2.6 FTIR

Surface analyses of adsorbed film, on the mild steel during the gravimetric tests in the presence of inhibitor were obtained by FTIR spectrum.

3 RESULTS AND DISCUSSION

3.1 Weight loss method

The inhibition effect of volatile corrosion inhibitor, on the carbon steel after 5Hrs exposure at 100% RH was discussed by weight loss method. Three different environments like, without immersion partially immersion and fully immersion with electrolyte. And calculate the corrosion rate and inhibition efficiency of the VCIs which is shown in the table 2, 3, 4 respectively. In all environments DCHAB shows that it is high and best inhibition on iron in the corresponding environments.

Table 2. Weight loss parameters for MS in presence of inhibitors after 5hrs exposure in

Corrosive medium

Serial no	Inhibitor	Weight loss (g)	Corrosion rate ($\mu\text{m/y}$)	Inhibition efficiency (%)
1	Control	0.0464	4.1	-
2	OTP	0.0271	2.4	42
3	OTS	0.0123	1.1	73.5
4	OTC	0.0103	0.9	78
5	OTB	0.0047	0.4	89
6	DCHAB	0.0023	0.2	95

Table 3. Effect of VCIs on MS after 5hrs exposure of partially immersion in corrosive medium

Serial no	Inhibitor	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate ($\mu\text{m/y}$)
1	Control	0.036	-	3.2
2	OTP	0.025	30	2.2
3	OTC	0.0088	75.5	0.8
4	OTS	0.0051	85	0.4
5	OTB	0.0032	91	0.3
6	DCHAB	0.0025	93	0.2

Table 4. Effect of VCI's on MS after 5hrs exposure of fully immersion at 100% RH in corrosive medium

Serial no	Inhibitor	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate ($\mu\text{m/y}$)
1	Control	0.017	-	1.5
2	OTC	0.0087	48.8	0.8
3	OTS	0.0062	63	0.5
4	OTP	0.0026	81	0.23
5	OTB	0.0028	83.5	0.24
6	DCHAB	0.0024	85.8	0.21

3.2 EIS

The nyquist plot of the carbon steel with this five inhibitor were drawn which is exposed about 5hrs in the H_2S environment is shown in the fig.1. It shows that the corrosion behaviour of mild steel in the sense of resistance to the corrosive medium in the presence and absence of inhibitor. The VCI's doesn't amend the mechanism dissolution of metal. Hence, it's purely depends on the charge transfer process. All experimental plots approximately have a semi-circular shape. The impedance measurement shows that the inhibition of the VCIs is characterised by increasing diameter of the arc which is acting the resistance R_{sol} is the solution resistance between the reference and working electrode. When the aggressive chemicals such as sulphur, water, ionic species permeate the inhibitor film to the active site of the metal, the corrosion of metals become measurable, so that is associated parameters, the double layer capacitance C_{dl} and charge transfer resistance R_{ct} can be estimated. The C_{dl} and R_{ct} values are shown in the table 5. And its shows that DCHAB having the R_{ct} , C_{dl}

value of 28445 ohm cm² and value of 6.4×10^{-5} $\mu\text{F}/\text{cm}^2$ respectively. Inhibition efficiency can be calculated by the equation (3).

Table 5. AC impedance parameter of MS after 5hrs exposure at 100% RH in Corrosive medium

Inhibitor used	R_{ct} (ohm cm ²)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	Inhibition efficiency (%)
Control	8625	68	-
OTP	10091	63	14
OTS	10926	59.5	21
OTC	12445	59	30
OTB	16099	49	46
DCHAB	36445	6.4×10^{-5}	73

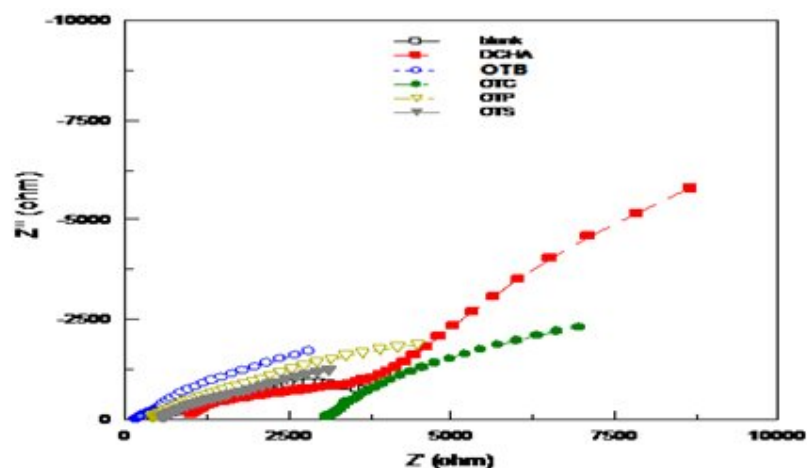


Figure 1. The impedance diagram for the blank and inhibitors after 5hrs exposure at 100% RH in Corrosive medium

Linear Polarization Resistance monitoring is an effective electrochemical method of measuring corrosion. Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream allows the calculation of the corrosion rate. LPR is most effective in aqueous solutions, and has proven to be a rapid response technique. In our studies the current produced by the blank i.e. without inhibitor is in the increasing order increase with increase in volt apply. But it is totally inversely related. The current produced by the best inhibitor is very low, when compare with other remaining inhibitors. With this account, which shows the best inhibition in the LPR is DCHA. Retained inhibitors shows less than this in the environment B which represented in the given below Fig.2. And the parameter value is given the below table. 6.

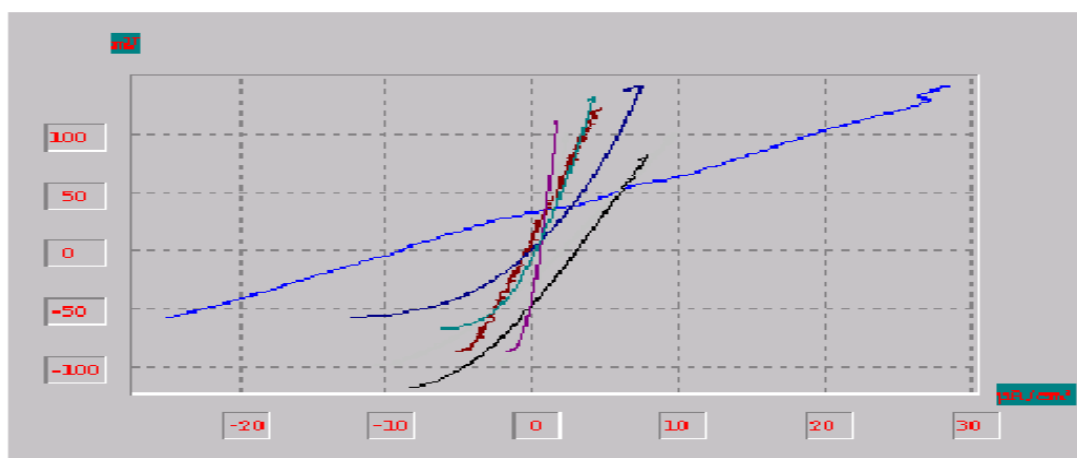


Figure 2. Linear Polarization resistance curve of the mild steel after 5 hrs exposure at 100% RH in corrosive medium

Blank; OTS; DCHAB; OTP; OTC; OTB

Table 6. Polarization parameters for MS in presence of VCI after 5 hrs exposure at

100% RH in Corrosive medium

Inhibitor	i_{cor} μ / cm^2	Tafel slope (mV/decade)		R_p K Ohm.cm ²	Inhibition efficiency %
		B_a	$-B_c$		
Control	28.9	172.8	173	2.59	-
OTP	3.1	362.3	61.1	6	56.8
OTS	2.4	245.7	98.6	14.47	82.1
OTC	0.75	302	66.8	12	78.4
OTB	1.5	352.8	58	22.68	88.5
DCHAB	4.5	167.2	156	31.52	91.7

3.4 Adsorption Isotherm

The values of $(\theta/1-\theta)$ Vs concentration of VCI inhibitor's were plotted, gives straight lines.

This follows Langmuir adsorption isotherm equation, given by $(\theta/1-\theta) = KC$.

Where K is equilibrium adsorption constant, C is the concentration of VPMA and θ is the surface coverage. The equilibrium adsorption constant, K, for the adsorption of the compound at different concentration were calculated from the slopes of straight lines fig.3. This suggests that the inhibitor prevents the contact of the metal with electrolyte by forming a barrier [24]. These straight lines suggest that the VCI's inhibitor for the mild steel in the H₂S environment has been obeyed the Langmuir Isotherm equation.

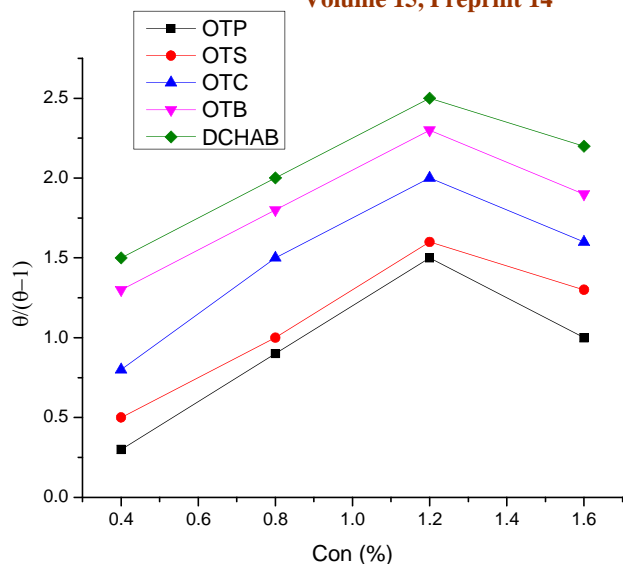


Figure .3 Langmuir Adsorption Isotherms of the inhibitor for mild steel in the presence of corrosive medium

3.5 FTIR

The synthesized VCI compounds and their inhibitive film formed on the surface of mild steel after 5hrs exposure at 100% RH in both corrosive medium has been studied using the FTIR spectral analysis. The mechanism for inhibition of corrosion on mild steel by the VCI compounds is clear from the spectral data obtained in the below table 7.

N-H, C=O, C-N bond of the OTB are shifted from 1551 to 1540 cm^{-1} , 1602 to 1642 cm^{-1} and 1165 to 1019 cm^{-1} . Similarly for the OTC's N-H, C=O, C-N bond are shifted from 1552 to 1513 cm^{-1} , 1632 to 1646 cm^{-1} , 1310 to 968 cm^{-1} . The OTS and OTP inhibitors of the N-H, C=O, C-N bond are shifted from the region 1568 cm^{-1} , 1562 cm^{-1} and its values were shifted to 1513 and 1539 cm^{-1} respectively. 1635 and 1643 cm^{-1} shifted to 1645 and 1700 cm^{-1} . The C-N bond value is shifted from 1103 and 1301 cm^{-1} to 1000 and 1012 cm^{-1} .

In DCHAB C-N, N=N bond shifted from 1109 and 1638 cm^{-1} to 1066 and 1633 cm^{-1} . N-H bond in the inhibitors are shifted from 3394 cm^{-1} to 3361 cm^{-1} .

From the above FT-IR investigation it shows that the octylamine derivated amide compounds such as OTB, OTC, OTP, and OTS all are having the lone pair electron containing atom like oxygen and nitrogen. In the amide compounds the nitrogen atom was donated their lone pair electron to the metal to form the Fe- inhibitor coordinated bond. It can be seen from the value that the C-N value was decreased and the C=O value increased.

But in the case of the DCHAB complex's there were availability of the 3 nitrogen atom to donate their lone pair electron to the metal atom in order to make the coordinated bond. The inhibition efficiency determine by the number of the electron donating atoms.

FT-IR spectra of the VCI compounds and iron specimens after 5 hrs film forming period were recorded and the corresponding figures are shown in the followings

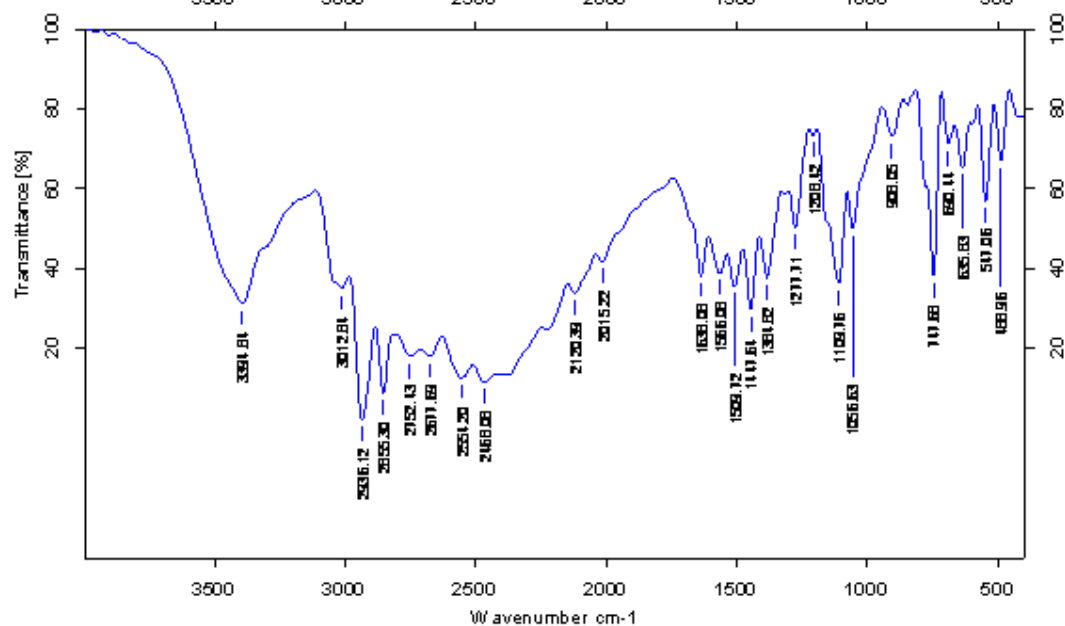


Figure 4. shows the FT-IR spectrum of the DCHAB inhibitor

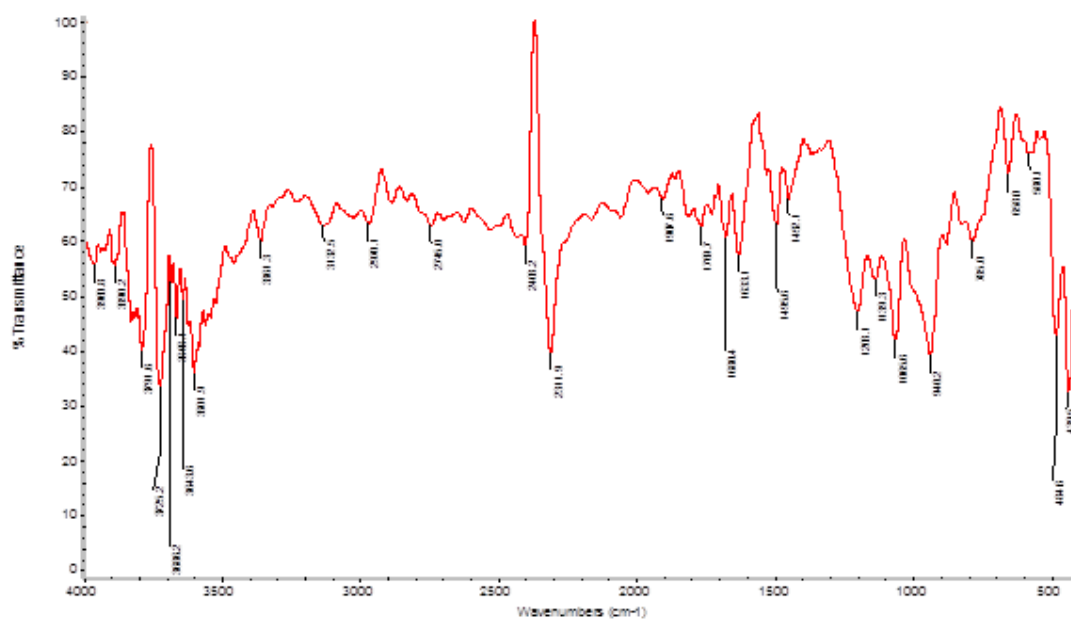


Figure 5. shows the FT-IR absorption spectrum for the DCHAB with metal in the environment

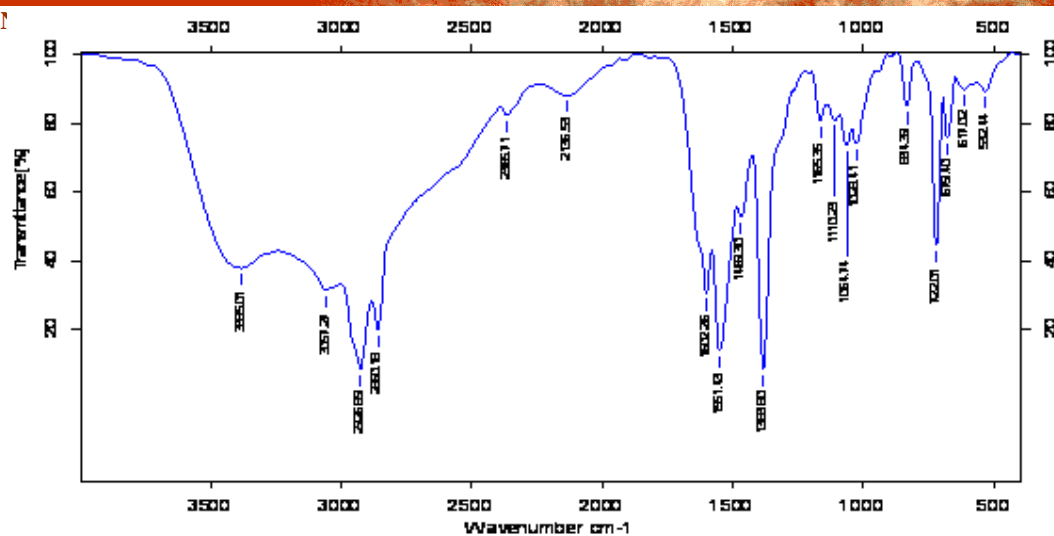


Figure 6. Shows the FT-IR spectrum of the OTB inhibitor

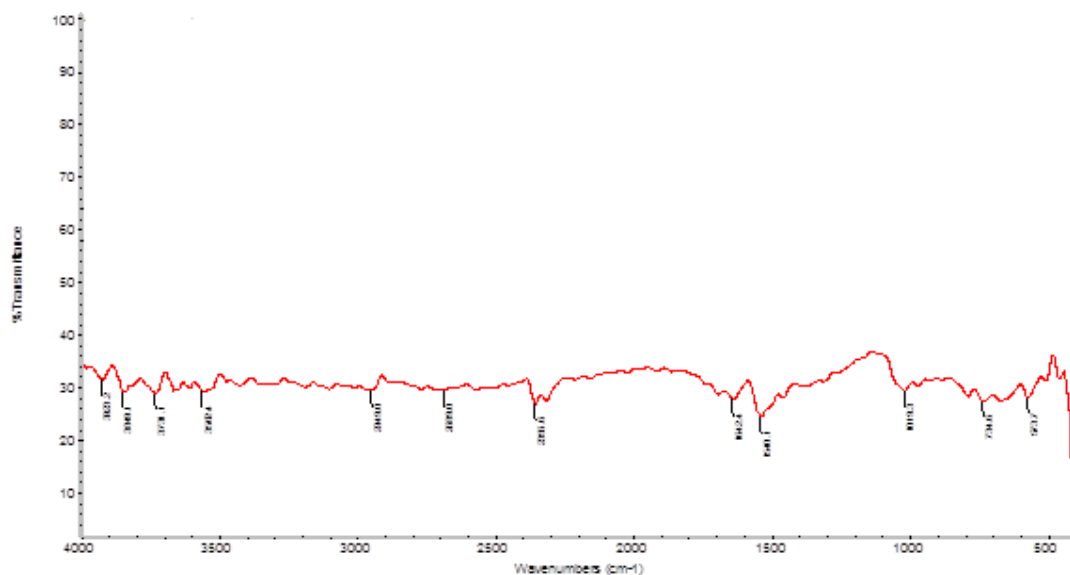


Figure 7. Shows the FT-IR absorption spectrum for the OTB with metal in the environment

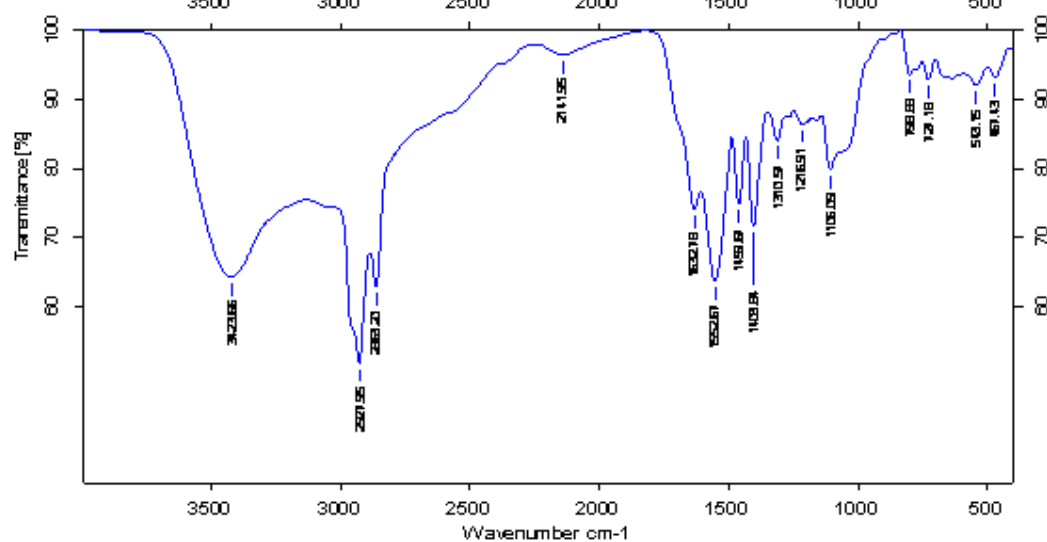


Figure 8 . Shows the FT-IR spectrum of the OTC inhibitor

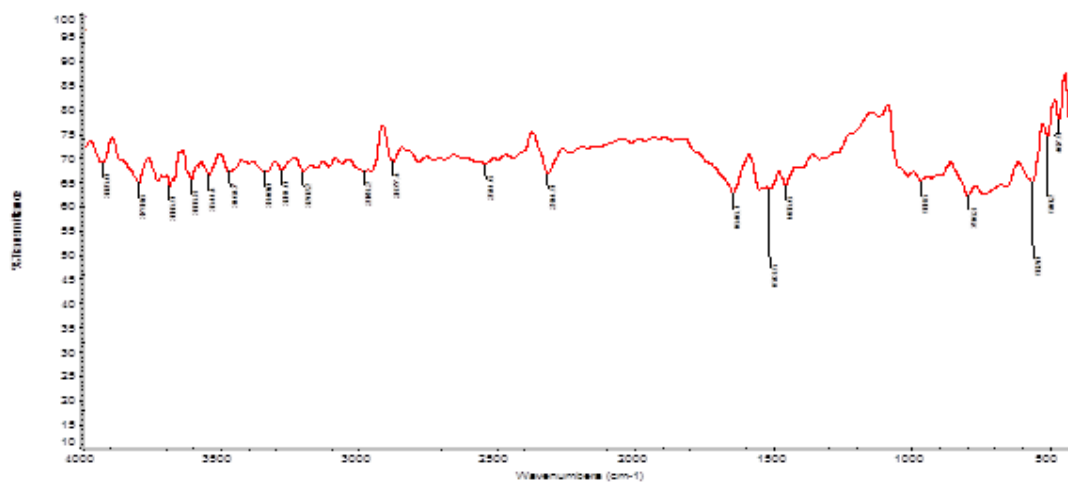


Figure 9. Shows the FT-IR absorption spectrum for the OTC with metal in the environment

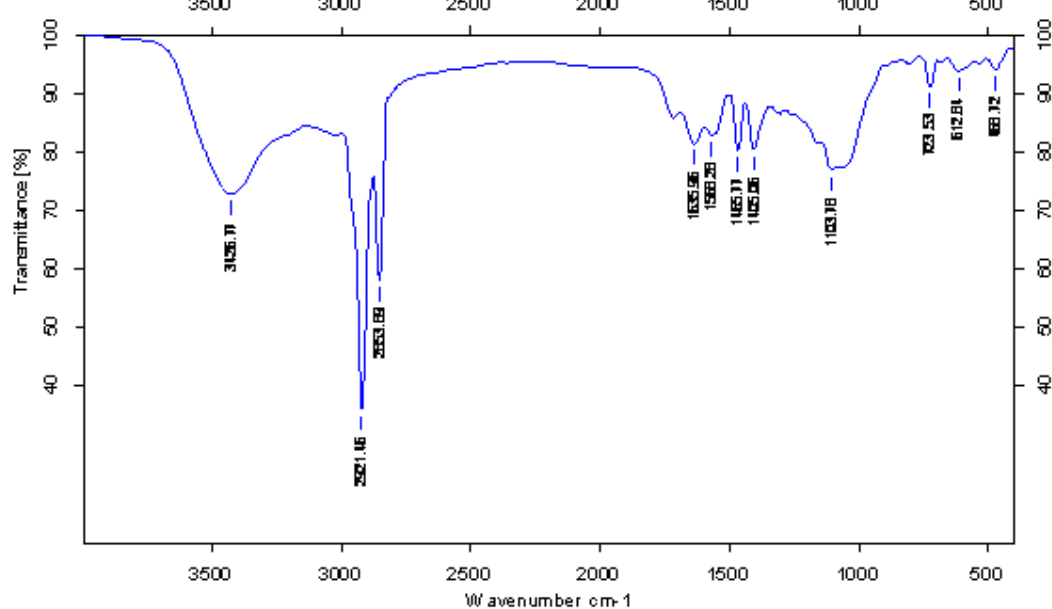


Figure 10. shows the FT-IR spectrum of the OTS inhibitor

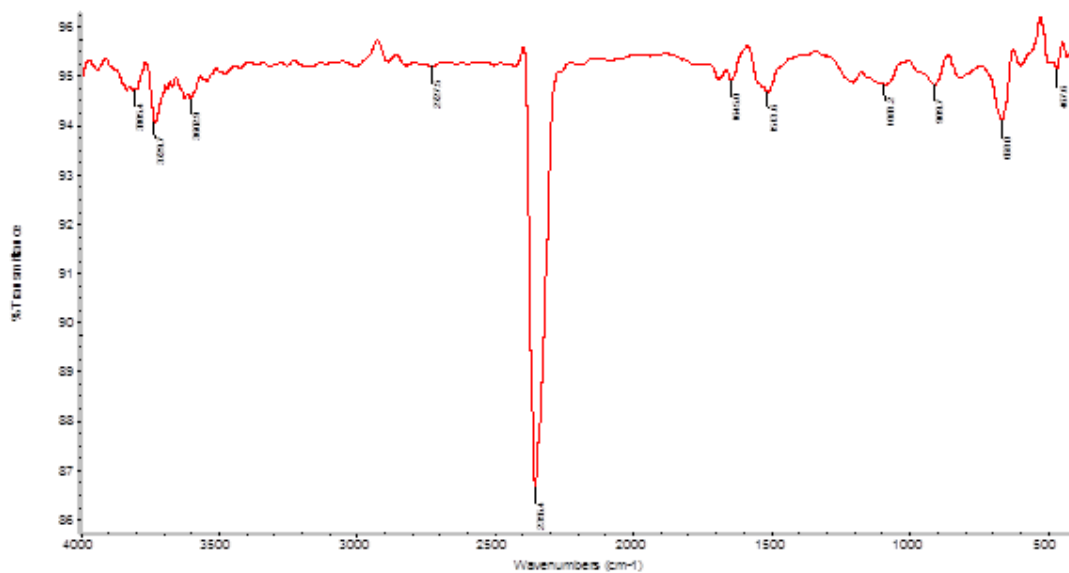


Figure 11. Shows the FT-IR absorption spectrum for the OTS with metal in the environment

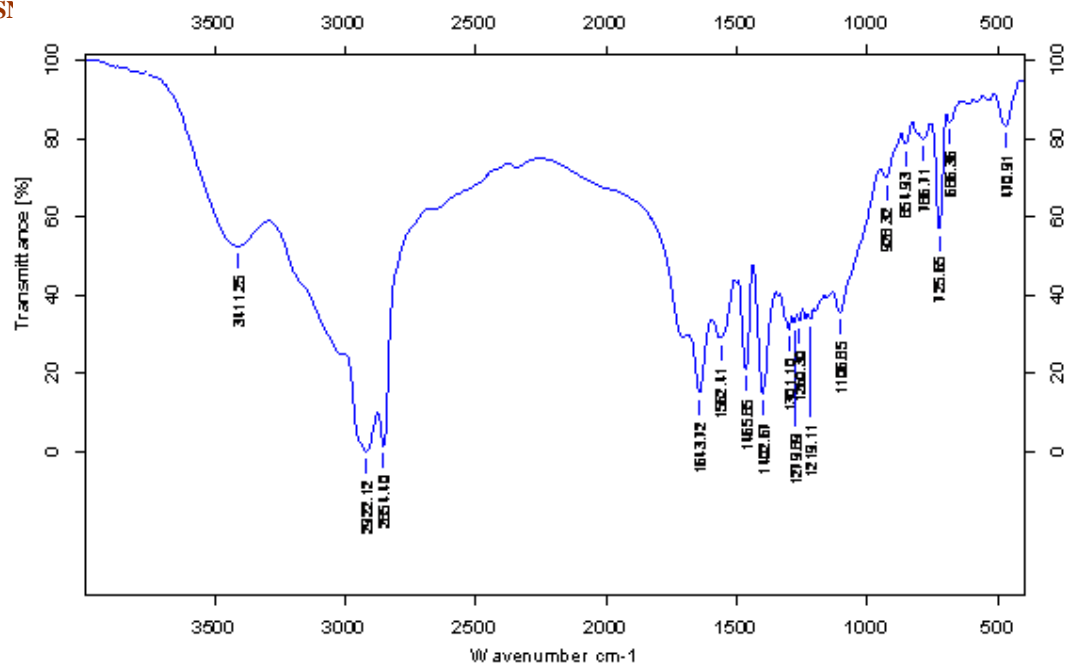


Figure 12. shows the FT-IR spectrum of the OTP inhibitor

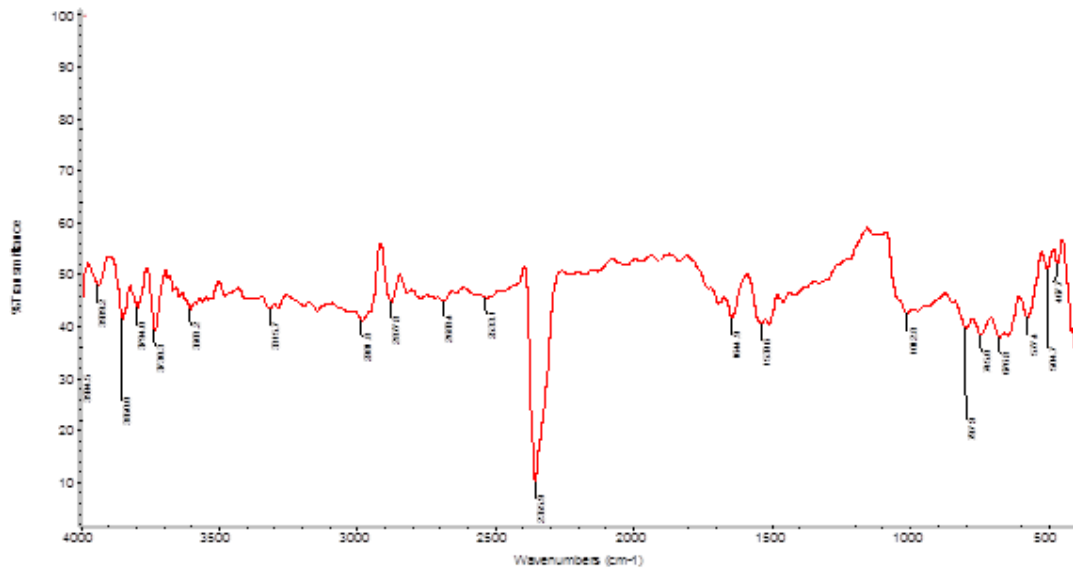


Figure 13. Shows the FT-IR absorption spectrum for the OTP with metal in the environment

Table 7. Absorption frequencies of FTIR spectra recorded for DCHA.BTZ and their surface film on MS after 5 hrs exposure at 100% RH in Corrosive medium B.

Name of the Inhibitor	Bond	Frequency Range Cm^{-1}	Measured Band	
			Inhibitor Cm^{-1}	MS Surface Film Cm^{-1}
DCHA.BTZ	C-N	1250-1020	1109	1066
	N-H	3500-3200	3394	3361
	N=N	1640- 1570	1638	1633
OTB	N-H	1600-1550	1551	1540
	C=O	1800-1600	1602	1642
	C-N	1360-1080	1165	1019
OTC	N-H	1600-1550	1552	1513
	C=O	1800-1600	1632	1646
	C-N	1360-1080	1310	968
OTS	N-H	1600-1550	1568	1513
	C=O	1800-1600	1635	1645
	C-N	1360-1080	1103	1000
OTP	N-H	1600-1550	1562	1539
	C=O	1800-1600	1643	1700
	C-N	1360-1080	1301	1012

4. CONCLUSION

1. The five inhibitors of OTP, OTS, OTC, OTB, DCHAB are synthesised and characterised.
2. In weight loss method, DCHAB shows its inhibition efficiency high in the three different environments.
3. In EIS analysis shows that the adsorbed protective layer on the metal surface act as hindrance for the metal dissolution in the H₂S environment.
4. And the LPR technique shows that the DCHAB has high polarized resistance 31.5Kohm. cm²
5. The surface analysis of the iron steel in the presence of inhibitor were investigated and identified by the FTIR.

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