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Study the Performance of Volatile Corrosion Inhibitors in Protection of Mild Steel in Cl_2 Gas Environments

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Abstract

Apprehend the corrosion of the mild steel (MS) in various environment has been studied. Amide like octylpalmamide (OTP), octylstearamide (OTS), octylcaprilamide (OTC) and dicyclohexylaminebenzotriazole (DCHA.BTZ) compounds exploited as VCI in this paper and tentative its corrosion rate and its inhibition power in corrosive Cl_2 gas medium. Weight loss mode used to calculate the former parameter. Surface characterization had been analyzed SEM and FTIR. Electro chemical studies of EIS and Tafel polarization and its parameter were computed by characterization. And find OTS was best VCI in Cl_2 medium via the above characterizations. The thermodynamic property adsorption isotherm has been calculated.

Keywords: Mild steel, volatile corrosion inhibitor, inhibition efficiency, corrosion rate, environment.

Introduction

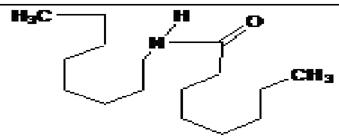
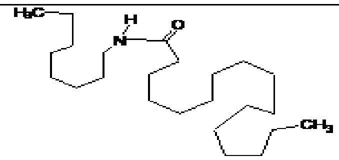
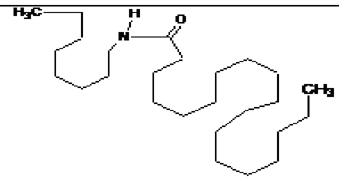
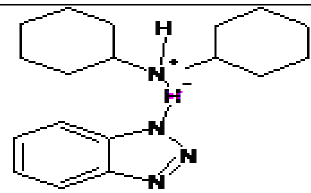
Corrosion is universal process which can't apprehend but can control. Day by day, the new chemical compounds were synthesized and being discover for the treatment of corrosion. Among them volatile corrosion inhibitor (VCI) which, could easily vaporized and give a best passive film on the mild steel. There are various investigation has been done on volatile corrosion inhibitor, by using aliphatic amine and salicylic acid and their salts. In this work, reveal the behavior of OTP, OTS, OTC and DCHA.BTZ in Cl_2 medium. The choice of the VCI is depends on its vaporization power and deposit on the surface of metal[1]. There are numerous investigations on corrosion inhibition studies by aliphatic amines, salicylic acid and their salts as vapor phase corrosion inhibitors for various industrial metals and alloys[2-5]. Benzoic hydride and its salt derivatives has been used VCI in at relative humidity atmosphere[6]. Inhibition effect depends on the inhibitor due some specialization fact like, chain length, size of the molecule and strength of bonding to the metal. Cyclohexylamine has high thermal stability in power plant and have VCI characteristic too, in pipeline. Aromatic compound such as, naphthalene has been a VCI at 250-350^{0}C in the HCl environment. Bayer synthesized cylcohexylamine and dicylcohexylamine as volatile corrosion inhibitor on iron[7]. Varity of aliphatic and alicyclic amine used as VCI[8]. Cyclohexylamine and dicycloheylamine used in an SO_2 environment as VCI[9]. Dicyclohexylamine also exhibit its volatile nature for an inhibitor for steel, copper and zinc[10]. The use of several VCI as an effective inhibitor has reported for carbon steel[11]. Many of amine carboxylate derivatives as VCI has discovered for different environmental condition[12]. From the literature survey, not much more article on corrosion behavior of mild steel in Cl_2 gas medium by using Amide as a volatile corrosion inhibitor (VCI). This article described the corrosion behavior of mild steel in a forth mentioned medium using SEM, FTIR, EIS and Tafel technique.

Material and Methods

Preparation of Specimens and Inhibitors: The specimen carbon steel's were made with following chemical composition of Carbon-0.07%, sulphur- nil, phosphorous-0.008%, silicon – nil, manganese -0.34%, Fe – balance. The synthesis of OTP, OTS, OTC and were prepared by the equimolar mixture of octylamine (Aldrich) with corresponding acids such as palmetic, stearic, caprylic acid(Merck) by stirring them at room temperature. And DCHA.BTZ was synthesised by incorporate dicyclohexylamine and benzotriazole (Aldrich). Finally, the synthesized inhibitors were characterized by FTIR. The molecular structure and weight of the amide inhibitor were shown below table-1.

Weight loss method: The metal specimen preparation and initial weighing procedure has been followed as before mentioned[15]. Cl_2 gas was passed though the chamber separately to create two different environments. The specimens were held by hooks in the desiccators over desiccators which consist of Cl_2 gas. This setup was kept in a thermostat water bath maintained at 50ºC. This arrangement produced a continuous under saturation of water vapors. One cycle included 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 and after the tests. The corrosion rate and inhibition efficiency (IE) was calculated as mentioned[14].

Table-1
Structures of VCI's

S.No	Structure	Molecular formula & weight	Vapour pressure (mmHg)	Name of VCI
1		$C_{16}H_{33}NO$ and 255.4393	2.5653×10^{-3}	OTC
2		$C_{24}H_{49}NO$ and 367.652	1.9667×10^{-3}	OTP
3		$C_{26}H_{53}NO$ and 395.7051	1.2740×10^{-3}	OTS
4		$C_{18}H_{29}N_4$ and 301.4498	1.253×10^{-3}	DCHA.BTZ

Potentiodynamic Measurement: The polarization measurement has been taken with help of three electrode system working. The potentio dynamic measurements were started by changing step wise 60mV/m on a PGP20IP potentiostat/galvanostatic. The anode potential could find at the steady potential. Tafel polarization drawn via interchanges the potential (E) and log I, the parameter b_a and b_c were evaluated.

Electrochemical Impedance Spectroscopy: The cell configuration of EIS was done by the electrochemical measurement unit solartron 1280b. Rct and Cdl value obtain from the difference between the values of real axis. They employed amplitude of ±20mV, frequency ranging 0.5Hz to 100 KHz.

Fourier Transformation Infrared Spectroscopic Studies (FTIR): Surface analyses of adsorbed film, on the mild steel during the gravimetric tests in the presence of inhibitor were obtained by FTIR (Model No - TENSOR 27 Software - OPUS version 6.5) spectrum.

SEM: For SEM image, $1cm^2$ specimen sample were taken, HITACHI S-3000H was used for scan the samples.

Results and Discussion

Weight loss method: The inhibition effect of volatile corrosion inhibitor, on the carbon steel after 5Hrs exposure in Cl_2 was discussed by weight loss method. And calculate the corrosion rate and inhibition efficiency of the VCIs which is shown in the table-2. In all environments OTS shows that it is high and best inhibition on iron in the corresponding environments.

Table-2
Effect of VCI's on MS in Cl_2 gas environment

S. No	Inhibitor	Weight loss (g)	Inhibition efficiency (%)	Corrosion Rate (µm/y)
1	Blank	8	Nil	0.7132
2	DCHA.BTZ	2.4	70	0.2139
3	OTP	2.1	74	0.1872
4	OTC	0.8	90	0.0772
5	OTS	0.1	98	0.0133

EIS Technique: The nyquist plot of the carbon steel with this five inhibitor were drawn which is exposed about 5hrs in the Cl_2 gas environment is shown in the figure-1. It shows that the corrosion behavior 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 characterized by increasing diameter of the arc which is acting the resistance. The Cdl and Rct values are shown in the table-3, which has highest inhibition efficiency in weight loss method for Cl_2 gas. And shows that OTS having highest value of Rct and Cdl value of 14571ohm cm^2, 3.508 x10^7μF/ cm^2 and than the other (which doesn't shown). The impedance spectrum shown figure-1, 2 Inhibition efficiency can also be calculated with this. Inhibition efficiency has been computed by equation-3.

Table-3
Electrochemical Impedance Studies in Cl_2 gas medium

Inhibitor used	R_{ct} Ohm cm^2	C_{dl} μF/cm^2	Inhibition Efficiency (%)
Blank	2389	3.005x10^{-5}	Nil
OTS	14571	3.508x10^{-7}	83

Tafel polarization Technique: Tafel Polarization monitoring is an effective electrochemical method of measuring corrosion. Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in environment allows the calculation of the corrosion rate. In our studies the current produced by the blank 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. With this account, which shows the best inhibition in measurement is OTS in Cl_2 gas environments. Retained inhibitors shows that less inhibition than the others (which doesn't show). Tafel graph took only for which represented highest inhibition in weight loss in the given below figure-3 the parameter values are given in below table-6.

Table-4
Polarization parameters for MS in presence of VCI after 5 hrs exposure at Cl_2 gas medium

Inhibitors	i_{cor} (μA/cm^2)	Tafel slope (mV/Decade)		R_p K Ohm.c m^2	Inhibition Efficiency (%)
		B_a	$-B_c$		
Blank	1.5	112	133	12.6	Nil
OTS	0.0399	218	187	82	85

Adsorption Isotherm: As mentioned weight % of VCI took for the demonstrations[13]. And it was obeyed the adsorption isotherm. Adsorption Isotherms of VCI on MS in both Cl_2 gas medium had shown in the figure-5. And it implied the maximum adsorption occurred 1.2%, at which maximum inhibition efficiency observed. Hence, we made the former Wt % for the all VCI to determine the inhibition efficiency in both Cl_2 and steam medium. The adsorption isotherm adhere the Langmuir adsorption isotherm.

SEM Spectral Details: SEM image reveals that the specimens are containing the corroded iron and unaffected specimen in their surface after exposure in Cl_2 gas environment. The amount of surface defects decreases by the inhibitor of OTS on the MS. The best coordinate bond layer distribution was observed on specimen containing inhibitor which shows in the figure-5 (magnification 1X). On comparing these two images, which is not having the inhibitor shows highly corroded particle on the MS surface. When compare with the first image there is no that much amount of corroded particle. Form the SEM analysis shows that OTS inhibitor is shows high inhibition efficiency among the others (which doesn't shown).

Table-5
Polarization parameters for MS in presence of 1.2wt % of VCI in Cl_2 gas medium

Inhibitors	i_{cor} (μA/cm^2)	Tafel slope (mV/Decade)		Rp (KOh m.cm^2)	Inhibition Efficiency (%)
		Ba	-Bc		
Blank	1.5	112	133	12.6	Nil
DCHA.BTZ	0.2636	197.7	155.3	45	72
OTP	0.16	137	170	58	78
OTC	0.05	219	66.8	63	80
OTS	0.0399	218	187	82	85

Table-6
Absorption frequencies of FTIR spectra recorded for OTS and in Cl_2 gas medium

Inhibitor	Bond	Frequency range cm^{-1}	Measured bond	
			Inhibitor cm^{-1}	MS Surface film cm^{-1}
OTS	N-H	3650-3200	3426	3604
	C=O	1800-1600	1635	1646
	C-N	1360-1080	1103	931

FT-IR Spectrum Analysis for OTS: The mechanism for inhibition of corrosion on mild steel by the VCI compounds is clear from the spectral data obtained in the below table-6. FTIR spectrums and tables are portrait for the best inhibitor, which has best inhibition in Cl_2 gas medium. It is seen from FTIR spectral data of VCI film formed on the metal surface in the Cl_2 medium, which the C-N stretching frequency of OTS has shifted from 1103 to 931cm^{-1}. It suggests that nitrogen atoms present in inhibitor are coordinated to MS resulting in the formation of inhibitor– Fe complex on metal surface. Similarly N-H, C=O absorption frequencies 3426, 1635cm^{-1}shifted to , 3604, 1646cm^{-1}, respectively in environment A. The shift in the value is due to the donation of lone pair of electrons of N atoms present in the VCI compound to Fe resulting in the formation of inhibitor-Fe complex. From the FTIR spectral analysis it is clear that inhibitor – Fe complex is formed on the metal surface. The higher inhibition efficiency of OTS may be due the presence of 2 nitrogen atoms when compared to other inhibitors. The lone pair electrons and then strong C-N sigma bond is present in the OTS formed thick non- visible complex on the metal surface to reduce the corrosion rate of metal in comparison with other VCIs.

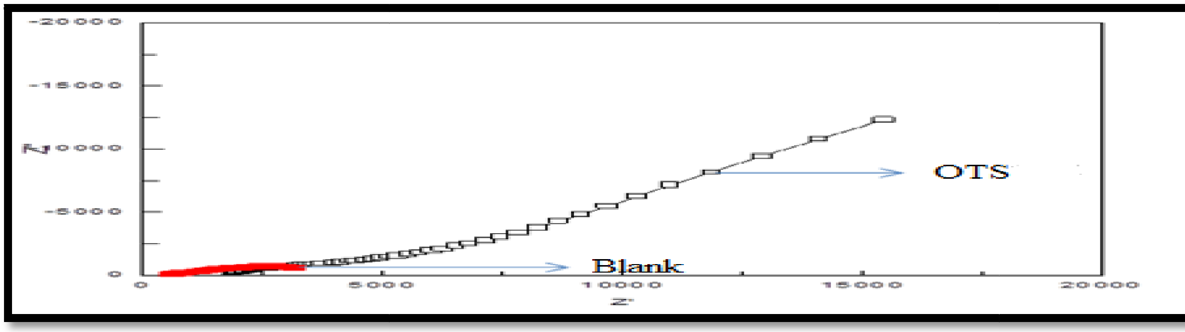


Figure-1
Impedance diagram for the blank and OTS in Cl_2 gas medium.

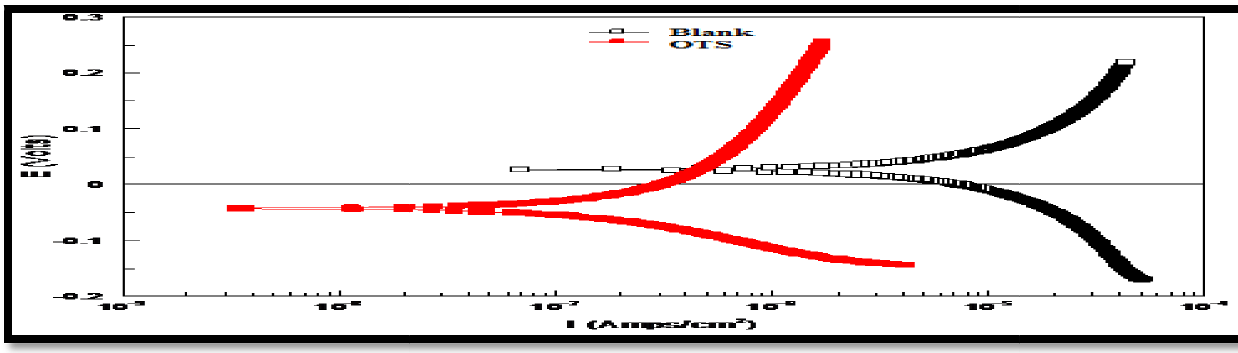


Figure-2
Tafel Polarization curve of Blank with OTS in Cl_2 gas medium

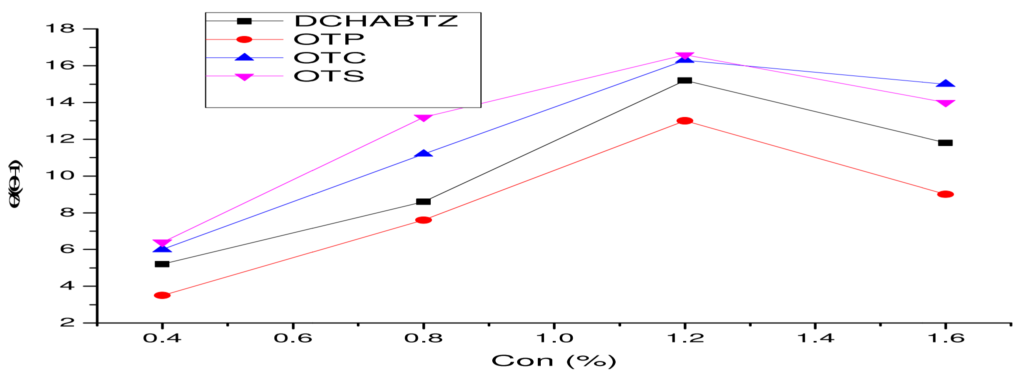


Figure-3
Adsorption isotherms in Cl_2 gas medium

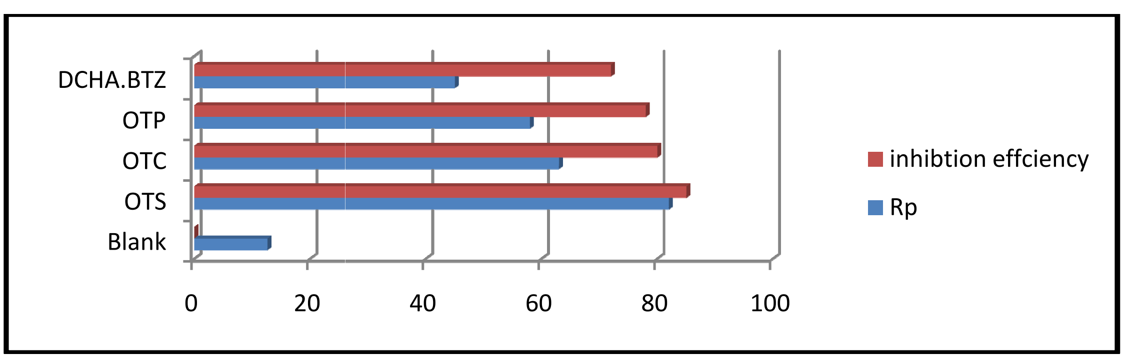


Figure-4
Rp and IE of inhibitors in Cl_2 medium

A **B**

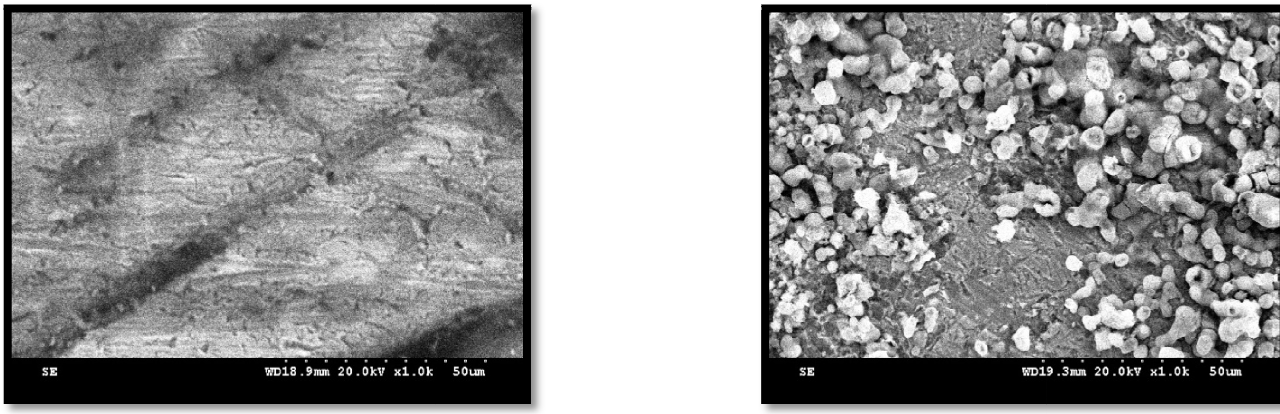


Figure-5 (A-B)
A- Specimen with OTS B-Blank

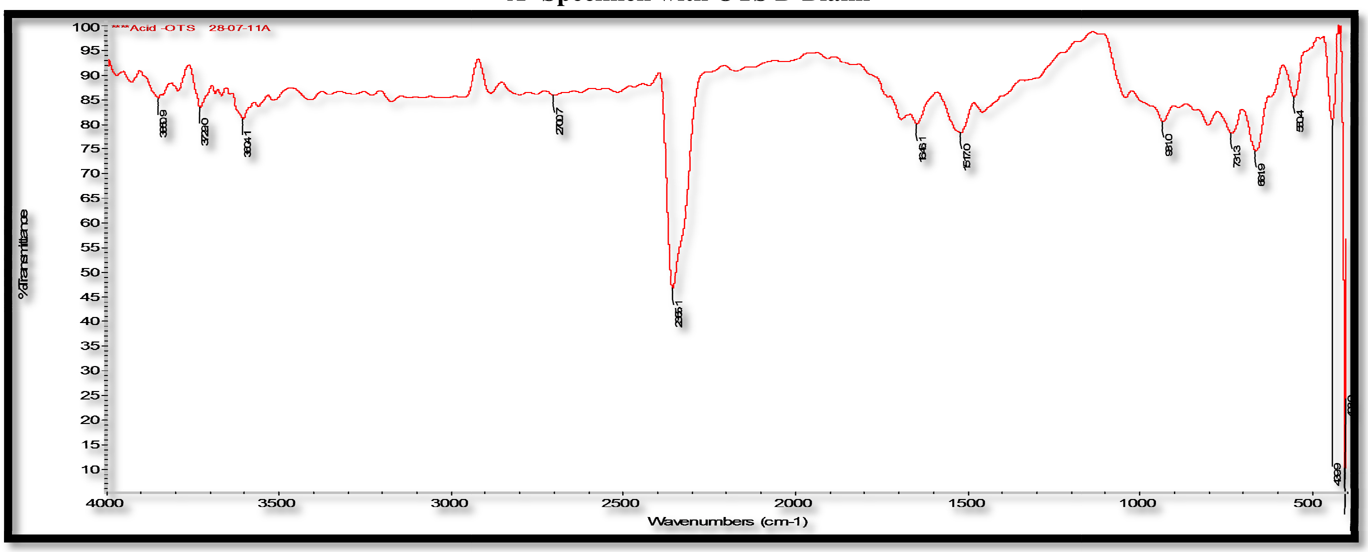


Figure-6 (a)
FT-IR adsorption spectrum of the OTS in Cl_2 gas environment

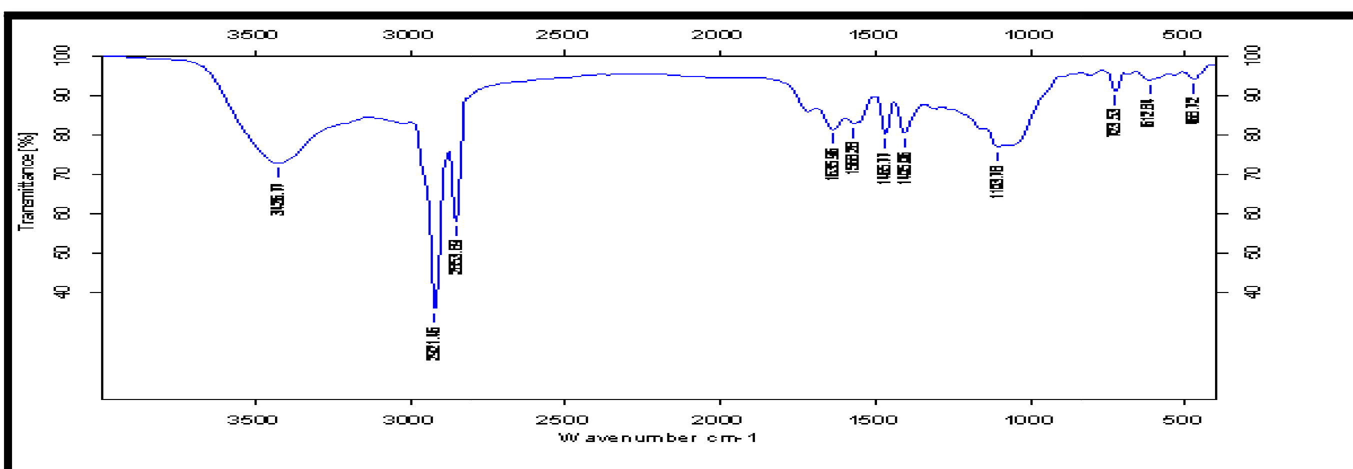


Figure-6 (b)
FT-IR spectrum of the OTS inhibitor

Conclusion

From this study, the above compound OTS, OTP, OTC and DCHA.BTZ could be used as a VCI. Even in the 1.2 % concentration gave the maximum adsorption power with the MS in the Cl_2 gas and steam medium. And maximum inhibition efficiency occurred at 1.2% concentration around 90% in both medium. And SEM analysis shows the best adsorption of inhibitor via the clear surface on the metal surface. Tafel explain that Rp, i_{cor} and IE value respectively, In Cl_2 gas medium OTC has 92 KOhm.cm^2, 2.3302 ×10^{-7} µA/cm^2 and 89%. Better than the blank and else other inhibitors. EIS study implied the best C_{dl} and Rct value of inhibitor were 3.654×10^{-5}µF/cm^2 and 9872 ohm.cm^2, 3.508×10^{-7}µF/cm^2 and 14571 ohm.cm^{2}of the inhibitors DCHA.BTZ and OTS in steam, Cl_2 gas medium respectively. FTIR accomplish how the adsorption took on the surface of the mild steel. And OTS vouch it non-bonded electron as former compound did. This could realized, from the FTIR data's

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