



## Effect of optimum concentration and temperature on inhibition of vasicine for mild steel corrosion in 1N hydrochloric acid

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### ABSTRACT

The recent trend of utilizing plant extract and pharmaceutical material as a corrosion inhibitor in the acidic medium has been increased. The isolation of vasicine from the extract of plant *Adhatoda vasica* (AD) shows a good inhibitive performance on mild steel material in 1N HCl. The isolation of vasicine compound was confirmed by characterization of  $C^{13}$ NMR, and LC- MS. Vasicine inhibition effect on mild steel corrosion and its mechanism by weight loss method, polarisation technique and electrochemical impedance method was carried out. Weight loss method indicated the inhibition efficiency of vasicine on corrosion of mild steel in 1N HCl solution increases with increase in concentration and decreases with rise in temperature. Polarization measurement show that a vasicine acts as mixed type inhibitor. The AC impedance study reveals that the charge-transfer process controls the corrosion of mild steel. The increase in activation energies of corrosion process in the presence of the vasicine retarded the rate of corrosion of mild steel in 1 N HCl solution. The protective film formed over the surface was confirmed by SEM Analysis. The vasicine compound reduces the permeation current. The nature of adsorption of the extract on mild steel surface follows Langmuir isotherm. The result of AC Impedance was correlating with the result of polarization measurement and Scanning electron microscopy (SEM)

**Keywords:** Mild Steel, Corrosion, Vasicine,  $C^{13}$  NMR and LC–MASS

### INTRODUCTION

Significant efforts are deployed to find a suitable compound to be used as corrosion pickling inhibitor to stop or slow the maximum attack of mild steel. Mild steel has been widely used alloy for industrial applications such as acid pickling, industrial cleaning, acid descaling etc. Acid solutions are mostly used in the industries for removal of rusts [3]. Use of inhibitors is one of the common methods in industries for protection of metallic corrosion. Synthetic inhibitors are an organic compound with N, O and S heteroatoms have higher electron density making them the reaction centers[2]. These compound are adsorbed on the metallic surface and block active corrosion sites. Most of the synthetic inhibitors have highly toxic hazard effects to both human beings and environment [1-4].

In the current study, the known hazardous effect of synthetic corrosion inhibitors has motivated scientists to use naturally present products as corrosion inhibitors as they are inexpensive, readily available and renewable sources of materials, environmentally friendly and ecologically acceptable and can be worked for inhibiting the corrosion of mild steel in acidic medium. Literature survey revealed that *Adhatoda vasica* extract has been in distilled water directly used as corrosion inhibitor [5]. And also explained the compound isolated from *Adhatoda vasica* extract was not used as a corrosion inhibitor. Hence, the vasicine isolated from *Adhatoda vasica* was used as corrosion inhibitor. Vasicine Compounds that contain  $\pi$ -bonds exhibit good inhibitive property by supplying electrons via the heteroatoms (N, S or O). A lot of works on plant extracts as green corrosion inhibitors have been done [1-11]. The effect of temperature on the corrosion behavior of mild steel with and without of the extract only was also studied. But they have not explained which compound act as corrosion inhibitors for mild steel corrosion in 1 N HCl at

various temperatures. In the present study deals with the effect of optimum concentration and temperature on inhibition of vasicine for mild steel corrosion in 1N Hydrochloric acid.

## EXPERIMENTAL SECTION

### 2.1 Isolation of vasicine extract from *Adhatoda vasica* leaves

*Adhatoda vasica* leaves was dried under the shadow for 20 days and then the leaf was powdered to a medium size particle. The powdered material was taken in 500 ml plastic bottle with 200 ml ethanol [4]. The resulting materials are kept shaker and shaking for 20 hr. 200 ml of material was concentrated under reduced pressure. The crude was acidified with for 2 hrs some black leaf precipitate was formed. Then the aqueous solution was basified using ammonia solution and extracted with chloroform, n-Hexane and Diether were also used using to remove non-polar impurities [4,5,6]. The isolated vasicine and the Structure of this compound were confirmed with  $^{13}\text{C}$ NMR and LC-MS

### 2.2. Preparation of specimens:

Mild steel specimens were cut to the size of 5 cm x 1 cm from the mild steel sheets having the following percentage composition as shown in the Table-1. The surface of the specimens was polished with various grades of emery papers ranging from 1/0 to 4/0. Further, the metal degreased with trichloroethylene specimens dried and stored in vacuum desiccator

**Table1: Composition of mild Steel**

Element	F	Ni	Mo	Cr	S	P	Si	Mn	C
Composition (%)	99.686	0.013	0.015	0.043	0.014	0.009	0.007	0.196	0.017

### 2.3. Spectral details of vasicine

#### 2.3.1. $^{13}\text{C}$ NMR spectrum

The  $^{13}\text{C}$  NMR is generated in the same fundamental as proton NMR spectrum. Only 1.1 % of naturally occurring carbon is  $^{13}\text{C}$  and an advantage because of less coupling. The number of signals explain us how many different C or set of equivalent C. The splitting of a signals explain us how many hydrogens are attached to each C. The chemical shift tells us the hybridization ( $\text{sp}^3$ ,  $\text{sp}^2$ ,  $\text{sp}$ ) of each carbon [12-15]. Splitting Pattern (N+1 rule): for each carbon the multiplicity of the signal depends upon how many protons are attached to it.

**Table-2 Typical  $^{13}\text{C}$  NMR Chemical Shift ranges**

ppm	hybridization	Kinds of compounds
0-70	$\text{Sp}^3$	Alkane( $\text{CH}_2$ )
70-100	$\text{Sp}^3$ and $\text{sp}$	C-O AND C-N
100-160	$\text{Sp}^2$	Aromatic C and C=C
160-210	$\text{Sp}^2$	Aldehyde and ketone(C=O)

#### 2.3.2 MASS spectrum

Electron ionization (EI) is a type of mass spectrometer ion source in which a beam of electrons interacts with a molecule M to form an ion according to



with a molecular ion  $\text{M}^{+\bullet}$ . The energy of the electron beam is typically 70 electron volts and the ionization process typically produces an extensive fragmentation of the chemical bonds of the molecule. The peak in the mass spectrum with the greatest intensity is called the base peak. More peaks may be visible with m/z larger than the molecule ion peak due to isotope distributions, called isotope peaks[16]. These peaks result from ions with life times shorter than the time needed to cross the distance between ionization chamber and the detector

### 2.4. Weight loss measurements

Mild steel specimens were immersed in triplicate in 100 ml of the test solutions (1N HCl) with and without the addition of an inhibitor of different concentrations. After the 1hr in terval periods, the test specimens were removed and their weight losses were determined using the precision electronic balance (precision  $\pm 0.0001$  g). The corrosion rate in mmpy was obtained from the following equation [18].

$$\text{Corrosion rate (mmpy)} = \text{KW/AT D} \quad (2)$$

Where,  $K = 8.76 \times 10^4$  (constant),  $W$  is weight loss in g,  $A$  is area in  $\text{cm}^2$ ,  $t$  is time in hr and  $D$  is density in  $\text{gm}/\text{cm}^3$  (7.86). The % of inhibition (IE) and the degree of surface coverage ( $\theta$ ) were calculated by the following equations

Where,  $K = 8.76 \times 10^4$  (constant),  $W$  is weight loss in g,  $A$  is area in  $\text{cm}^2$ ,  $t$  is time in hours and  $D$  is density in  $\text{gm}/\text{cm}^3$  (7.86)

$$\text{Inhibition Efficiency (\%)} = \frac{W_a - W_p}{W_a} \times 100 \quad (3)$$

$$\text{Surface coverage (\theta)} = \frac{W_a - W_p}{W_a} \quad (4)$$

Where,  $a$  and  $p$  are corrosion rates in the absence and presence of the inhibitor.

### 2.5. Electrochemical measurements

Electrochemical measurements like Potentiodynamic Polarization studies and electrochemical AC Impedance method were carried out using (CHI 608 D/E model) with the computer controlled electrochemical measurement system. Three compartment cell with a mild steel as the working electrode, calomel electrode as a reference electrode, and platinum as an auxiliary electrode was used in 1N HCl absence and presence of inhibitor concentration of 800ppm. The working electrode was allowed for 15 min in the test solution for stabilization of corrosion potential before recording the polarization curves. All the experiments were performed at  $30 \pm 1$  °C and each value is the mean of triplicate experiments [17,19].

### 2.6. Surface analysis

The test specimens were immersed in 100 ml of conc. HCl with vasicine for 24 hr. After termination of the experiment, the specimens were washed with distilled water, dried and examined for their surface morphology and adsorbed molecules using Scanning Electron Microscope (SEM) [20].

## RESULTS AND DISCUSSION

### 3.1. $\text{C}^{13}\text{NMR}$ spectral data analysis

$\text{C}^{13}\text{NMR}$  spectra were recorded on 400F (400MHz) NMR spectrometer using  $\text{CDCl}_3$  as solvent and TMS as internal standard ESI-MS spectrum in Atmospheric (pressure ionization) showed molecular ion peak at  $m/z$ .

#### 3.1.1 $\text{C}^{13}\text{NMR}$ spectral analysis

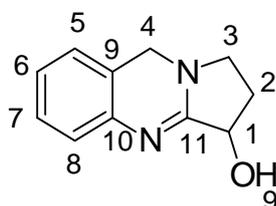


Fig.1:  $\text{C}^{13}\text{NMR}$  structure of vasicine

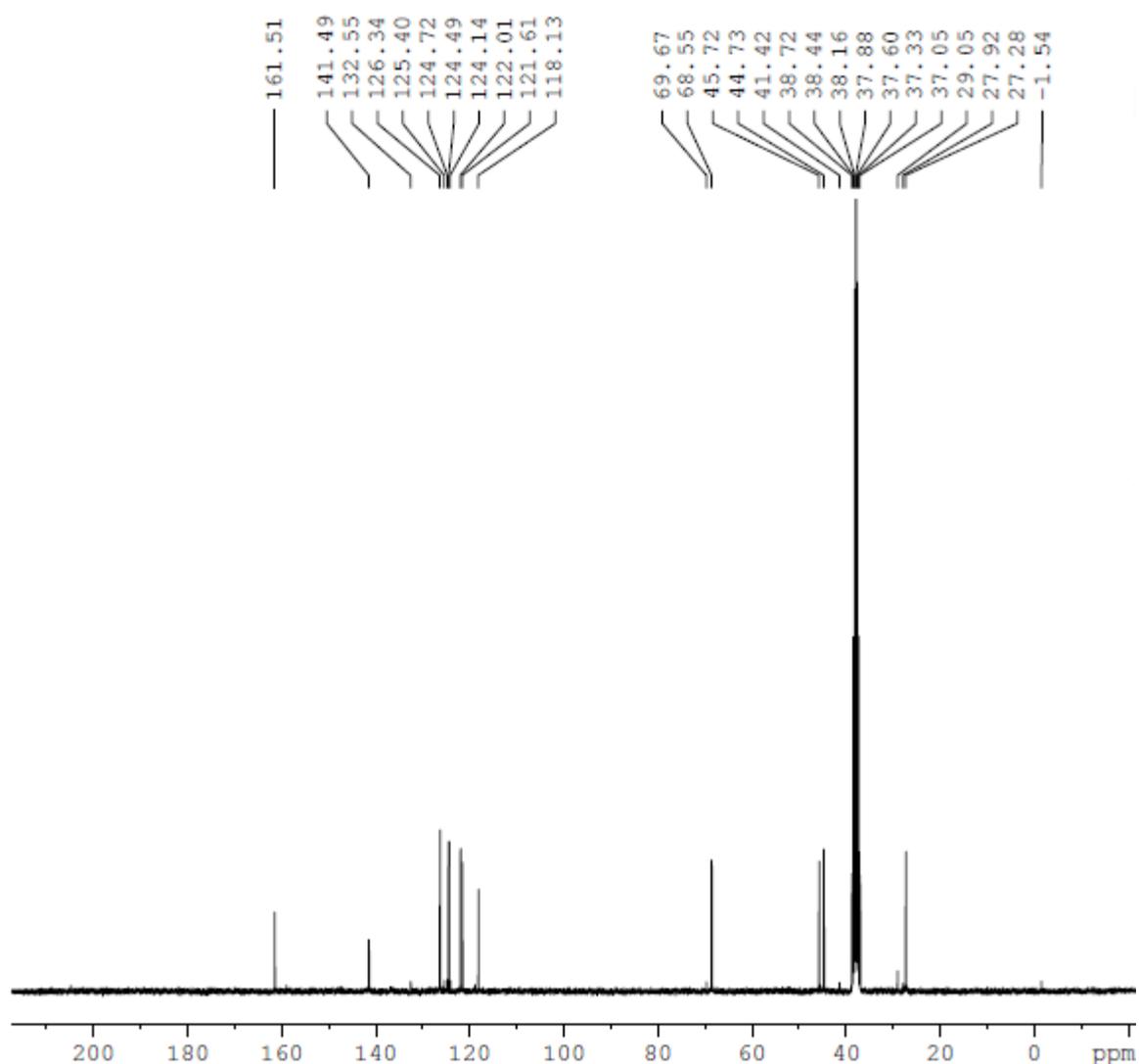
The  $\text{C}^{13}\text{NMR}$  spectral data are given in Table-4. The  $\delta$  values of the C-13 NMR of vasicine were in the  $\delta$  values for vasicine are:  $\delta$  27.92 (C-2), 44.73 (C-4), 45.72 (C-3), 69.67 (C-1), 118.13 (C-8), 126.34 (C-5), 124.14 (C-6), 126.34 (C-7), 124.49 (C-9), 141.49 (C-10) and 161.51 (C-11). It is concluded from the  $\text{C}^{13}\text{NMR}$  data that the structure of vasicine isolated from *Adhatoda vasica* was confirmed by shown fig.2

Table-3  $\text{C}^{13}\text{NMR}$  chemical shift assignment for vasicine

Position	Experimental values ( $\delta$ - ppm)	Data from the literature ( $\delta$ - ppm)
C-2	27.92	28.8
C-4	44.73	47.30
C-3	45.72	48.1
C-1	69.67	70.2
C-8	118.13	119
C-5	126.34	125.7
C-6	124.14	124.0
C-7	126.34	128.0
C-9	124.49	123.6
C-10	141.49	142.3
C-11	161.51	163.9

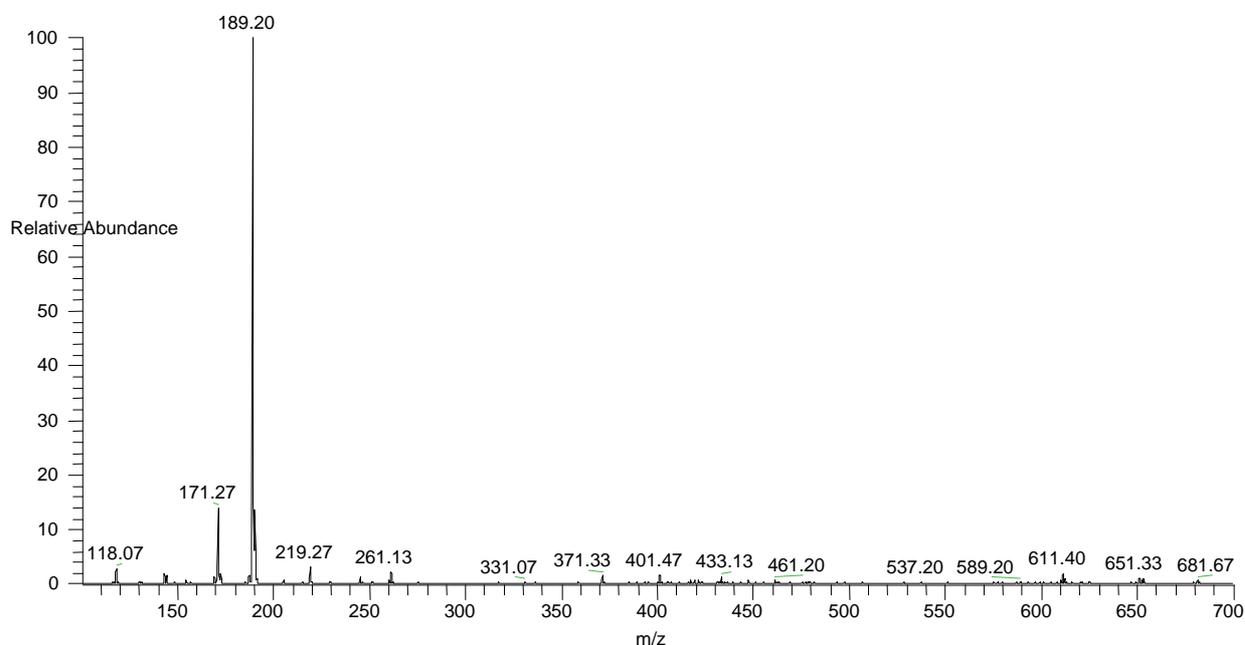
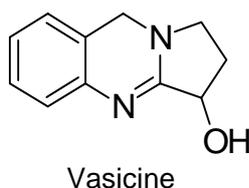
Table-4  $C^{13}$  NMR spectral data of vasicine

Peak value ppm	Peak type	No.of carbon atoms assigned	Position in the structure
27.92	singlet	1	2
44.73	singlet	1	4
45.72	singlet	1	3
69.67	singlet	1	1
118.13	singlet	1	8
126.34	singlet	1	5
124.14	singlet	1	6
126.34	singlet	1	7
124.49	singlet	1	9
141.49	singlet	1	10
161.51	singlet	1	11

Fig.2:  $C^{13}$  NMR spectrum of vasicine

### 3. 2 LC-MASS spectral analysis

The isolated vasicine compound was also confirmed by LC- mass spectra. Mass spectra of the isolated vasicine compound revealed a molecular ion peak at 189 (Fig.3). The mass spectral fragmentation patterns, as well as the molecular weight observed. Mass spectral analysis (+ve Mode – source was used as reagent gas. Standard vasicine (molecular weight 188, M + 1 peak at 189) isolated vasicine (molecular weight 188, M + 1 peak at 189), Atmospheric( pressure ionization) of vasicine showed molecular ion peak at m/z 189.20 [M - H] The mass spectrum[21-23].



**Fig. 3: Mass spectral of vasicine**

### 3.3 Weight Loss studies.

Inhibition efficiency of isolated vasicine on mild steel corrosion in 1N HCl at 303 K by weight loss studies is shown in Fig. 4. The various corrosion parameters such as corrosion rate, surface coverage and inhibition efficiency (IE) were obtained from weight loss method for mild steel in 1 N HCl without and with different concentrations of the vasicine compound ranging from 200 ppm to 1000 ppm at 303K and listed in Table 5. It can be seen from Table 5. IE was found to be increased with an increase in the concentration of isolated vasicine and then decreases. The maximum inhibition efficiency 99.03 % was obtained at 800 ppm of vasicine that is due to the formation of a protective layer by added vasicine and then decreased even up to 1000 ppm. [7-17].

**Table-5 Inhibition efficiency of isolated vasicine on mild steel corrosion in 1N HCl at 303 K by weight loss studies**

Conc. vasicine ppm	Rate of corrosion(mmpy)	Surface coverage( $\theta$ )	Inhibitor efficiency(%)
Blank	30	-	-
200	1.99	0.9289	93.37
400	1.60	0.9523	94.67
600	1.51	0.9696	94.97
800	0.29	0.9903	99.03
1000	0.96	0.9784	96.80

### 3.4 Effect of immersion time

The effect of immersion period from 1hr to 24 hrs was studied by using weight loss method. The inhibition efficiency was decreased from 99.03 to 91.51%. At an optimum concentration (800ppm) of vasicine on corrosion inhibition efficiency of mild steel in 1 N HCl at 303K Vasicine was found that for 1 hr the maximum inhibition efficiency 99% was found to be for 1 hr. Though 91.51% inhibition efficiency was obtained even at 24 hr inhibition efficiency, 91.51% was obtained [24].

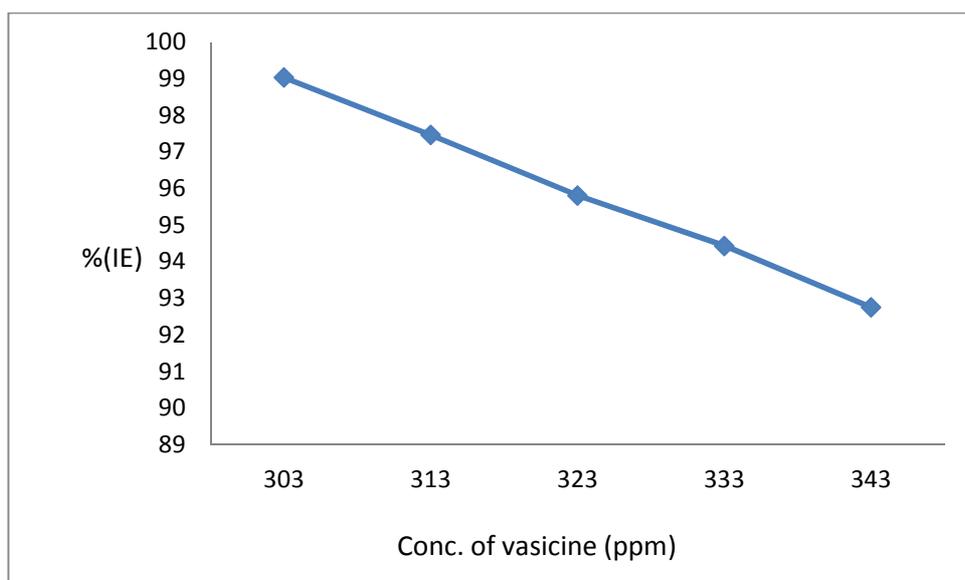


Fig 4: Inhibition efficiency of vasicine on mild steel corrosion in 1N HCl at 303 K by Weight Loss Studies

Table-6 Effect of immersion time on percentage inhibition efficiency of mild steel in 1N HCl at 303 K in the presence of an optimum concentration (800ppm) vasicine

system	Inhibition Efficiency (%)								
	Time(hr)								
	1	2	3	4	5	6	12	18	24
800 ppm of vasicine	99.03	98.14	97.03	96.00	95.36	94.75	82.97	92.01	91.51

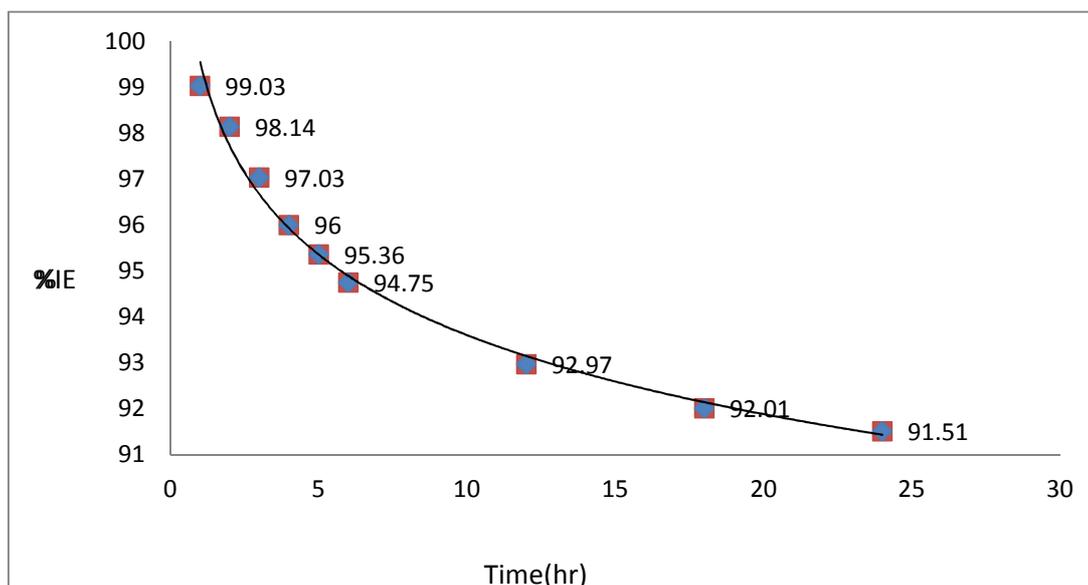


Fig.5 Effect of immersion time on percentage inhibition efficiency of mild steel in 1N HCl at 303 K in presence of an optimum concentration (800ppm) of vasicine

### 3.5 . potentiodynamic polarization studies

The polarization curves for mild steel in 1N HCl ( $30 \pm 1^\circ\text{C}$ ) with and without optimum concentration of vasicine are shown in Fig.6. The electrochemical parameters derived from the curves are given in Table 7. The  $E_{\text{corr}}$  values are marginally shifted in the presence of vasicine. It is observed that the optimum concentration of vasicine has a little influence on values of anodic Tafel constant and appreciable influence on the values of cathodic Tafel constant, indicating and that inhibitor may change the mechanism cathodic reation and may not affect anodic dissolution mechanism. The appreciable increase in the bc values with increase in the vasicine concentration indicates that H evolution is suppressed due to the blockage of sites at the metal surface by the vasicine molecules. This can be attributed to the formation of very closely adherent adsorbed film on the metal surface [25]. Supplementary evident shows that the adsorption of the vasicine molecules on the metal surface , makes a physical

barrer for the mass and charge transfer, leading to the high degree of protection to the metal surface. It was observed that with increase in concentration of vasicine from 100 ppm to 1000 ppm, the maximum inhibition efficiency of 99.67% was observed for vasicine at an optimum concentration of 800 ppm

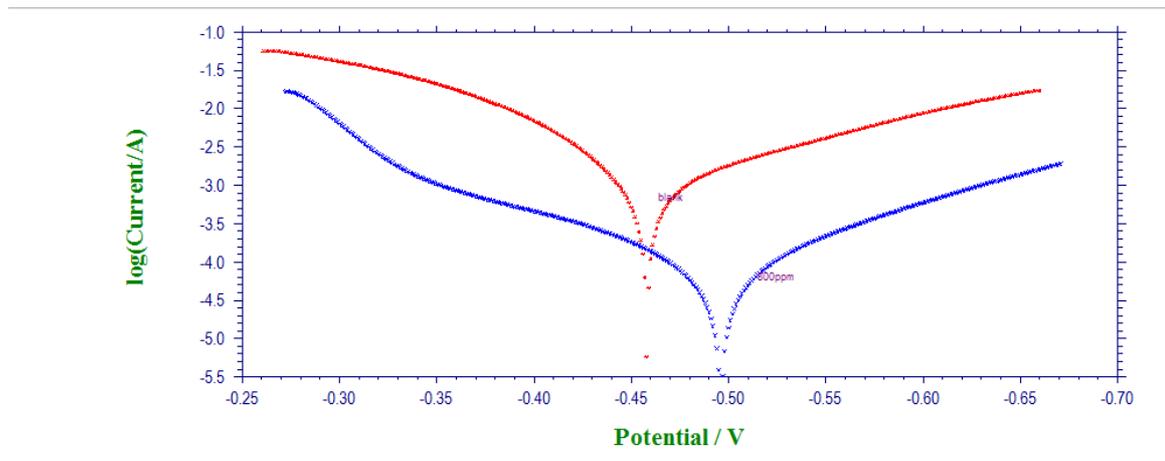


Fig.6: The potentiodynamic polarization curves for mild steel in 1N HCl with vasicine

Table-7 Potentiodynamic Polarization parameters for mild steel in 1 N HCl with vasicine 303K

Concentration of vasicine ppm	$E_{corr}$ (mV)	Tafel slopes (Mv/dec)		$I_{corr_2}$ ( $A/cm^2$ )	inhibition efficiency(%)
		ba	Bc		
Blank	-0.453	5.50	3.56	1550	-
800	-0.498	6.16	4.36	29.92	99.67

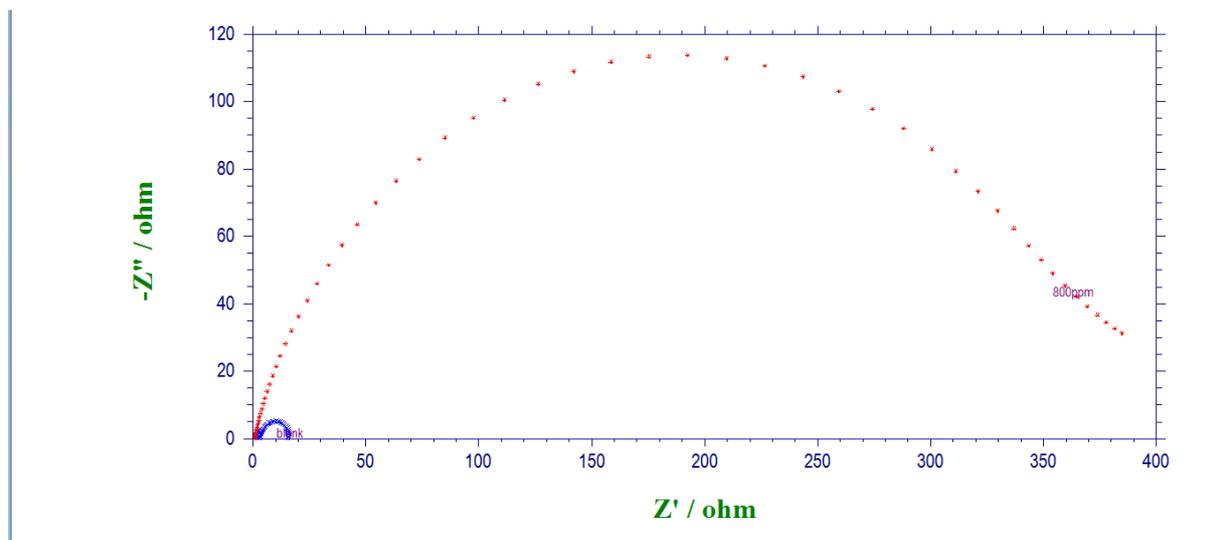


Fig.7: AC Impedance curves for mild steel in 1N HCl with vasicine

### 3.6 Electrochemical AC Impedance Method.

Impedance diagram obtained for the frequency range from 10 kHz to 0.01Hz with respect to the OCP potential of mild steel in 1N HCl with and without of vasicine are shown in fig.6.AC Impedance parameters derived from Nyquist plots were given in table-7.it is observed that the value of charge transfer resistance was found to be increased with increase in concentration of vasicine and the double layer capacitance (Cdl) values are decreased with increase in inhibitor concentration. A significant charge transfer resistance is associated with slowly corroding systems [26]. Also, improved inhibitor protection is associated with a decrease in metal capacitance [27]. The decrease in double layer capacitance which resulted from a decrease in the local dielectric constant and an in the thickness of the electrical double layer, confirmed vasicine as active adsorption at the metal interface [28]. The semicircular appearance of impedance diagram indicates that the corrosion of mild steel is controlled by a charge transfer of mild steel is mainly controlled by a charge transfer between the inhibitor molecule and mild steel surface [29]. The optimum inhibition efficiency was found to be 98.26 % in 1N HCl for 800 ppm of vasicine at 303 K.

Inhibition efficiency obtained in AC impedance method is in good agreement with polarization and weight loss methods.

**Table-8 Electrochemical AC Impedance parameters for mild steel in 1 N HCl with vasicine at 303 K**

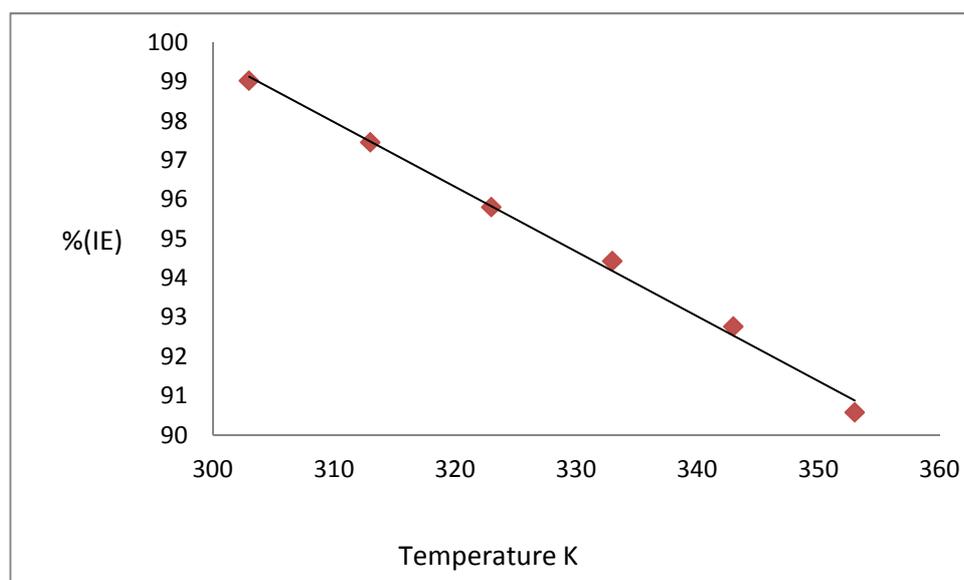
Concentration of vasicine(ppm)	$R_{ct}(\Omega \text{ cm}^2)$	$C_{dl}(F/\text{cm}^2)$	Inhibition efficiency (%)
Blank	12	231.02	-
800	390	83.20	98.26

### 3.7 Effect of temperature

The rate of corrosion and inhibition efficiency for an optimum temperature of mild steel in 1N HCl at 303 K to 353 K with an optimum concentration (800ppm) of vasicine are shown in fig.10. The corrosion rate was found to be very less (0.75 mmpy) at the optimum concentration 800 ppm at 303 K and with temperature increasing from 303K to 353K [2].The corrosion rate was found to be increased from 0.75 to 4.12 mmpy which indicates that there is a common increase in weight loss as the temperature increased from 303K to 353 K and the inhibition efficiency was found to be decreased slightly from 99.03% to 90.57% but it was able to withstand even at 353 K (Table- 9). This is by the general rule guiding the rate of chemical reactions which says that chemical reaction increases with increasing temperature [30].

**Table -9 Effect of temperature for optimum concentration (800ppm) of vasicine on corrosion of mild steel in 1 N HCl at different temperatures obtained by weight loss method**

Temperature/ K	Rate of corrosion(mmpy)	Inhibitor efficiency(%)
303 K	0.75	99.03
313 K	1.56	97.46
323K	1.91	95.81
333K	2.24	94.43
343 K	3.31	92.76
353 K	4.12	90.57



**Fig.10: Effect of temperature on percentage inhibition efficiency of mild steel in 1N HCl at 303 K to 353 K in presence of an optimum concentration (800 ppm) of vasicine**

### 3.8 Mechanism of corrosion inhibition by vasicine

The Arrhenius plot for mild steel immersed in 1N HCl solution in without and with an optimum concentration (800 ppm) of vasicine as shown in fig.11 The plot of the graph for corrosion rate versus the inversely proposing of absolute temperature gave a straight line. According to the Arrhenius equation [31]

$$\ln r = A - E_a / RT \quad (5)$$

Where  $r$  is the corrosion rate,  $A$  is the constant frequency factor and  $E_a$  is the activation energy. The values of activation energy ( $E_a$ ) [32] for the corrosion process in the without and with of an optimum concentration of vasicine were calculated from the Arrhenius equation

$$\text{Log} \frac{K_2}{K_1} = \frac{E_a}{2.303 R} [1/T_1 - 1/T_2] \quad (6)$$

Where K1 and K2 are the corrosion rates at temperatures T1 and T2 respectively.

The free energy of adsorption ( $\Delta G^\circ$ ) used to find out the interaction of adsorption molecules and metal surface, was calculated using the equation.

$$\Delta G^\circ = -RT \ln (K/55.5) \quad (7)$$

The value of 55.5 is the concentration of water in solution expressed in molar. The value of K can be calculated using the equation [32].

$$K = \theta / (1-\theta) C \quad (8)$$

The enthalpy of adsorption ( $\Delta H$ ) was calculated using the equation

$$\Delta H = E_a - RT \quad (9)$$

and the entropy of adsorption ( $\Delta S$ ) was calculated using the equation

$$\Delta G^\circ = \Delta H - T\Delta S \quad (10)$$

The calculated values of activation energy ( $E_a$ ), enthalpy of adsorption ( $\Delta H$ ), the free energy of adsorption ( $\Delta G^\circ$ ) and entropy of adsorption ( $\Delta S$ ) are shown as Table 10. The activation energy  $E_a$  was found to be 19.40 KJ mol<sup>-1</sup> for 1N HCl solution and increased to 29.60kJ mol<sup>-1</sup> in the presence of vasicine. The adsorbed vasicine provided a physical barrier to charge and mass transfer, leading to a reduction in corrosion rate. The higher value  $E_a$  in the presence of vasicine compared to that without of the vasicine was attributed to physical adsorption [33]. The negative sign of free energy of adsorption indicates that the adsorption of *vasicine* on mild steel surface is a spontaneous process [9]. It is well known that the value of  $\Delta G^\circ$  around -20 KJ mol<sup>-1</sup> or lower are consistent with the electrostatic interaction between organic charged molecules and the charged metal (physisorption) and those around -40 KJ mol<sup>-1</sup> or higher involved charge sharing or transfer from the organic molecules to the metal surface to form a coordinate bond (Chemisorption) [34]. In this case, the  $\Delta G^\circ$  values were in the range -12.13 to -12.96 KJ mol<sup>-1</sup> and hence the adsorption could be Physisorption. The positive values of enthalpy of adsorption ( $\Delta H$ ) suggest that the reaction is endothermic and the adsorption of the vasicine on mild steel surface takes place. The entropy of adsorption ( $\Delta S$ ) remained a positive and this is due to the formation of an ordered stable layer of the vasicine on mild steel. Positive values of entropy indicates that the reaction was spontaneous and feasible [35]. The inhibition mechanism involved is due do the adsorption of N and OH present in vasicine on surface of the metal and forming a dense protective thin layer on the mild steel

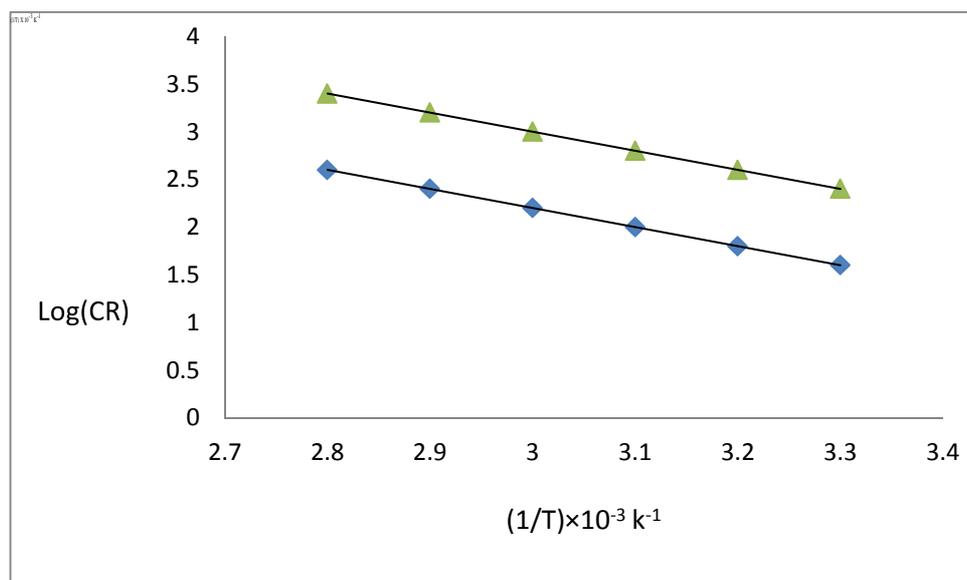


Fig. 11: Arrhenius plots for mild steel immersed in 1N HCl solution without and with of an optimum concentration (800 ppm) vasicine

**Table-10** Calculated values of activation energy (Ea), enthalpy of adsorption ( $\Delta H$ ), free energy of adsorption ( $\Delta G^\circ$ ) and entropy of adsorption ( $\Delta S$ ) without and with an optimum concentration of vasicine

System	Temp. (K)	Ea (KJ mol-1)	$\Delta G^\circ$ (KJmol-1)	$\Delta H$ (KJmol-1)	$\Delta S$ (KJmol-1)
Blank	303	19.4	-	12.74	-
	313		-	12.16	-
	323		-	11.91	-
	333		-	11.82	-
	343		-	11.53	-
800 ppm of vasicine	303	29.6	-12.13	29.21	0.121
	313		-12.17	32.11	0.190
	323		-12.52	35.43	0.176
	333		-12.61	36.32	0.121
	343		-12.83	37.15	0.113
	353		-12.96	39.45	0.101

### 3.9. Adsorption isotherms

Fundamental information on the interaction between the inhibitor and mild steel surface coverage( $\theta$ ) are investigated by the adsorption isotherms with optimum concentrations of vasicine in 1N HCl at room temperature have been used to explain the best isotherm to determine the adsorption process. The value of the surface coverage ( $\theta$ ) was calculated using the relationship [19,32]

$$\theta = [\text{IE}\%] / 100 \quad (11)$$

The values of various isotherm Langmuir, Temkin, ElAwady, Frumkin, Freundlich, Flory-Huggins are to fit. The best fit was obtained with Langmuir adsorption isotherm as suggested by the plot between  $C/\theta$  and  $C$  (Fig -12), and the linear correlation coefficient of the fitted data was close to 1, indicating that the adsorption of the vasicine compound obeys the Langmuir adsorption isotherm the following equation [33]

$$[C/\theta] = C + [1/K_{\text{ads}}] \quad (12)$$

Where  $C$  is the inhibitor concentration and  $K_{\text{ads}}$  is the equilibrium constant for adsorption, desorption process of the inhibitor molecules on the metal surface  $K_{\text{ads}}$  values were calculated from the intercept of the plot for the adsorption process. The adsorption and the standard free energy ( $\Delta G_o$  ads) is related to constant equilibrium  $K_{\text{ads}}$  by the following equation [34]

$$K(\text{ads}) = [1/55.5] \exp [-\Delta G_o(\text{ads})/RT] \quad (13)$$

Where the value 55.5 in the above equation is the molar concentration of water in solution in mol/L and the negative sign of  $\Delta G_o$  ads indicated that adsorption of the vasicine compound was spontaneous process [30]. The adsorption of the vasicine can be presented as a substitution adsorption process between the organic molecules in aqueous solution ( $\text{Org}_{\text{aq}}$ ) and the water molecules ( $\text{H}_2\text{O}_{\text{ads}}$ ) on mild steel surface [35].



Where  $x$  is, the number of water molecules replaced by one vasicine compound and  $x$  is assumed to be independent of coverage or charge on the electrode. Since the adsorption of the vasicine on the metal surface is conforming to Langmuir isotherm, there is no interactive or repulsive force between the adsorbed molecules on mild steel surface [31].

**Table-11: Langmuir adsorption isotherm for adsorption of vasicine on mild steel in 1N HCl**

Conc. vasicine (ppm)	Rate of corrosion (mmpy)	Surface coverage( $\theta$ )	$C/\theta$	Inhibitor efficiency (%)
Blank	30	-	-	-
200	1.99	0.9389	213.0152	93.37
400	1.60	0.9501	412.0083	94.67
600	1.51	0.9612	624.2197	94.97
800	0.29	0.9923	806.2078	99.03
1000	0.96	0.9786	1021.868	96.80

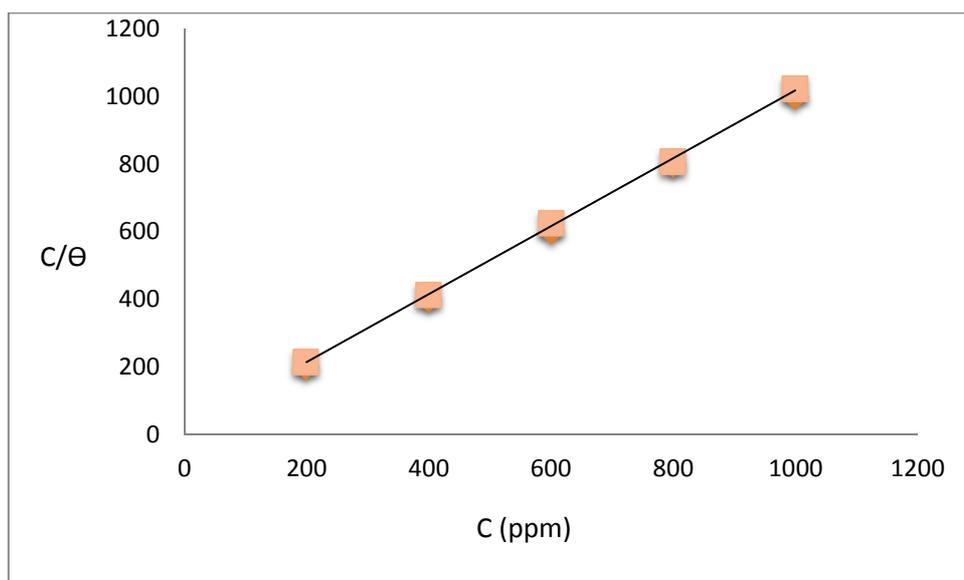


Fig .12: Langmuir adsorption isotherm for adsorption of vasicine on mild steel in 1N HCl

### 3.10 Surface Examination Studies.

Surface analysis was carried out by SEM technique to observe the surface conditions of the mild steel in contact with 1N HCl solution. The surface of mild steel specimens without and with vasicine concentration immersed for 24 h at 303 K was studied using Scanning electron microscope (SEM) with the magnification of 1000x specimens [34]. In the presence of the inhibitor, the micrographs show less evidence of pitting compared to without inhibitor for vasicine but shows a surface. This result is due to the adsorption of inhibitors compound around the pits. The inert film blocks the active site present on the mild steel surface. Thereby retorted the corrosion process.

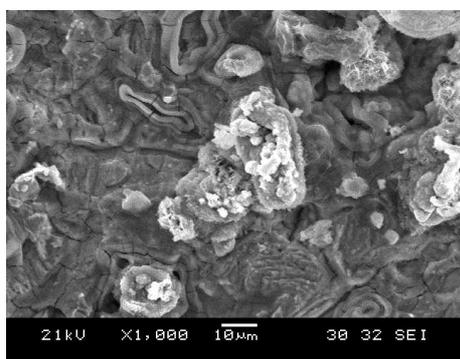
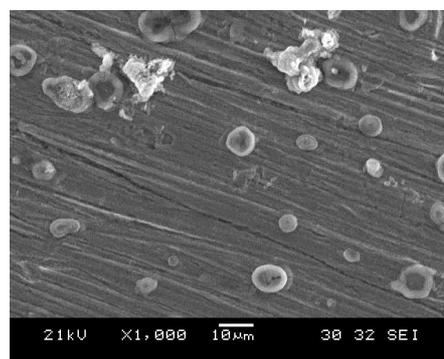


Fig.13a SEM micrographs of mild steel in 1N HCl



13.b SEM micrographs of mild steel in 1N HCl with vasicine

## CONCLUSION

The following conclusions were made from the studies.

- The structure of isolated vasicine was confirmed by  $C^{13}$ NMR and LC–MASS spectral analysis.
- Inhibition efficiency of the vasicine compound on corrosion of mild steel in 1N hydrochloric acid decreases from 99.03% to 90.57% with rise the temperature from 303K to 353K.
- vasicine acts as efficient corrosion inhibitor on mild steel in 1N hydrochloric acid.
- The maximum inhibition efficiency 99.03 % was obtained at optimum concentration 800ppm of vasicine that is due to the formation of a protective layer by the added vasicine and then decreased even up to 1000 ppm.
- vasicine was found that for an immersion period of 1 hr the maximum inhibition efficiency 99%
- Inhibition efficiency obtained in Electrochemical AC impedance analysis was in good agreement with polarization studies, showed that the examined vasicine acted as a mixed type inhibitor.
- The maximum Inhibition efficiency 99% of vasicine was observed with respect to inhibitor up to 800 ppm in all the cases.
- The adsorption of vasicine was consistent with the Langmuir adsorption isotherm.

- SEM study confirms that the inhibition of corrosion of mild steel is through adsorption of vasicine on the surface of mild steel and these studies also supplement the results of electrochemical techniques.

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