Int. J. Electrochem. Sci., 8 **(2013)** 10851 - 10863

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Mannich Bases Derived from Melamine, Formaldehyde Alkanoleamines as Novel Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Medium

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Received: 29 May 2013 / *Accepted:* 9 July 2013 / *Published:* 1 August 2013

The corrosion inhibition of mild steel using two new Mannich bases namely 2,2',2''((((1,3,5-triazine-2,4,6-triyl)tris(azanediyl)tris(Methylene)tris(azanediyl)triethanol (INH-1) and 2,2',2'',2''',2''''((((1,3,5-triazine-2,4,6-triyl)tris(azanediyl)tris(Methylene)tris(azanediyl)hexaethanol (INH-2) has been investigated using weight loss and electrochemical methods . The INH-1and INH-2 showed maximum efficiency of 92% and 95% at 25ppm concentration respectively. Potentiodynamic polarization suggests that the inhibitors depict mixed type behavior. The Electrochemical impedance spectroscopy (EIS) measurement shows that inhibitors were adsorbed at mild steel surface and obeyed Langmuir adsorption isotherm. Various thermodynamic parameters were also determined to investigate the mechanism of corrosion inhibition. The results obtained from weight loss and electrochemical methods are in good agreements.

Keywords: Acid corrosion, Mild steel, Thermodynamic parameter, EIS

1. INTRODUCTION

Inhibited acidic solutions are extensively used in several industrial processes during acid pickling, acid cleaning, acid descaling and ocidization of oil well etc. [1]. It has been reported that most of the well-known organic inhibitors are heterocyclic compounds containing N, O, and S [2–12]. The planarity and lone pairs of electrons present on N atoms are the important structural features that determine the adsorption of these molecules on the metal surface. A few Mannich bases has been studied as corrosion inhibitors in our group [13,14].

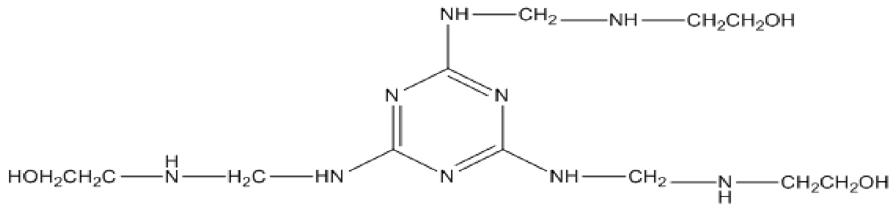
The objective of the present work was to develop improved version of inhibitors by reacting with formaldehyde and alkanoleamine and to studied their inhibiting action on mild steel surface in 1M HCl by weight-loss and electrochemical methods.

The choice of these compounds as corrosion inhibitor is based the following consideration, they can be readily synthesized from commercially available materials and easily adsorbs on mild steel surface through lone pair (N& O) and π-electrons present in these inhibitors. Both the Mannich bases molecules contain nine nitrogen atoms π e- and aromatic ring through which they can easily adsorbed on metal surface and bring about inhibition. Further, literature survey reveals that these compounds have not been used previously as corrosion inhibitors. Therefore, the investigated Mannich bases can be successfully used as corrosion inhibitors for mild steel in acid medium.

2. EXPERIMENTAL

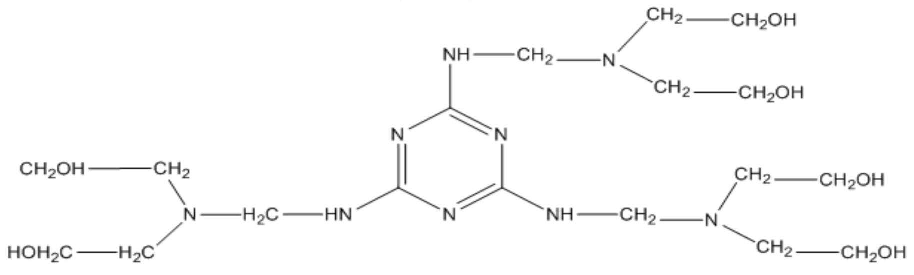
2.1. Inhibitor synthesis

Mannich bases were synthesized by refluxing the aqueous formaldehyde, melamine and amine (ethanolamine and diethanolamine for synthesis of INH-1 and INH-2 respectively), in a molar ratio of [melamine]: [formaldehyde]: [amine] = 1:3:3 for 4-5 h, followed by water distillation under vacuum at 65-75 ^{0}C [15]. The name and structural formula of the synthesized inhibitors are given below:



2,2',2''-((((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tris(methylene))tris(azanediyl))triethanol

(INH-1)



2,2',2'',2''',2'''',2'''''-((((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tris(methylene))tris(azanetriyl))hexaethanol

(INH-2)

Figure 1. Structure and names of both Mannich bases

2.2. Materials

The mild steel specimens have composition (wt. %): Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr 0.050%, Ni 0.050%, Al 0.023%, and Cu 0.135% was used in present study . The mild steel coupons were abraded successively with emery papers from 600 to 1200 mesh/in grade then washed with double distilled water, rinsed in acetone and finally dried. All experiments were carried out in unstirred solutions of 1M HCl which was prepared by dilution of analytical grade HCl (37%) with double distilled water. The specimens having area 2.5 × 2.0 × 0.025 cm^3 were used for weight loss experiments and electrochemical measurements were carried out using a 7.5 cm long stem of mild steel with an exposed area of 1.0 × 1.0 cm^2 covering the remaining portion with epoxy resin.

2.3. Test Solution

The test solutions of inhibitors were prepared by dissolving Mannich bases in 1 M HCl in concentrations ranges from 5 ppm to 25 ppm. Double distilled water was used for dilution.

2.4. Weight loss method

Weight loss measurements were performed on mild steel sample by immersing it in the absence and presence of different concentrations of inhibitors at 308K for 3h duration in 1M HCl solution. The inhibition efficiency (η%) and surface coverage (θ) was calculated using the following equations:

$$\eta\% = \frac{C_{\mathrm{R}} - C_{\mathrm{R(i)}}}{C_{\mathrm{R}}} \times 100 \qquad (1)$$

$$\theta = \frac{C_{\mathrm{R}} - C_{\mathrm{R(i)}}}{C_{\mathrm{R}}} \qquad (2)$$

where C_R and $C_{R(i)}$ are the corrosion rate values in absence and presence of inhibitor respectively. The corrosion rate (C_R) of mild steel in acidic medium was calculated by using following equation:

$$C_{\mathrm{R}} = \frac{W}{At} \qquad (3)$$

where, W is weight loss of mild steel coupon (mg), A is the area of the coupon (cm^2) and t is the exposure time (h).

2.5. Electrochemical impedance spectroscopy

The EIS tests were performed at 308±1K in a three electrode assembly. A saturated calomel electrode (SCE) was used as a reference and a platinum foil was used as counter electrode. All the potentials were measured versus SCE. The electrochemical impedance spectroscopy measurements were performed using a Gamry potentiostat / galvanostat with a Gamry framework system based on ESA 400 in a frequency range 10^{-2} Hz – 10^{5} Hz under potentiodynamic conditions with amplitude of 10 mV peak to peak, using AC signal at Ecorr. Gamry applications include software DC105 for corrosion and EIS300 for EIS measurements and Echem analyst version 5.50 software packages for data fitting. The experiments were carried out after 30 minutes of immersion in the test solution without de-aeration and stirring.

The inhibition efficiency was calculated from the charge transfer resistance values using following equation:

$$\eta(\%) = \frac{R_{\mathrm{ct}}^{'} - R_{\mathrm{ct}}^{0}}{R_{\mathrm{ct}}^{'}} \times 100 \qquad (4)$$

where, $R^{\mathrm{i}}_{\mathrm{ct}}$ and R^{0}_{ct} are the charge transfer resistances in presence and absence of inhibitor, respectively.

2.6. Potentiodynamic polarization

The electrochemical behavior of mild steel specimen in absence and presence of different concentrations of inhibitors was studied by recording anodic and cathodic Potentiodynamic polarization curves. Measurements were performed in 1M HCl solution containing different concentrations of the tested inhibitors by changing the electrode potential automatically from −250 to +250 mV vs. OCP at a scan rate of 1 $\mathrm{mVs^{-1}}$. The electrochemical parameters such as corrosion current densities (i_{corr}) were derived from extrapolating the anodic and cathodic linear segments of Tafel Polarization curves.

The inhibition efficiency was evaluated from the measured i_{corr} values using the relationship:

$$\eta(\%) = \frac{i_{\mathrm{corr}}^{0} - i_{\mathrm{corr}}^{'}}{i_{\mathrm{corr}}^{0}} \times 100 \qquad (5)$$

where, i^{0}_{corr} and i^{i}_{corr} are the corrosion current densities in absence and presence of inhibitor, respectively.

2.7. Linear polarization measurement

The linear polarization study were carried out from cathodic potential of -0.02V vs. OCP to an anodic potential of +0.02 V vs. OCP at a sweep rate of 0.125 $\mathrm{mVs^{-1}}$ to study the polarization resistance (R_{p}) in 1 M HCl solution in absence and presence of different concentrations of inhibitor. Polarization resistance (R_{p}) was evaluated from slope of the curve in the vicinity of the corrosion potential.

The inhibition efficiency was calculated from the polarization resistance values by the relationship as follows:

$$\eta\% = \frac{R_{\mathrm{p}}^{\mathrm{i}} - R_{\mathrm{p}}^{0}}{R_{\mathrm{p}}^{\mathrm{i}}} \times 100 \qquad (6)$$

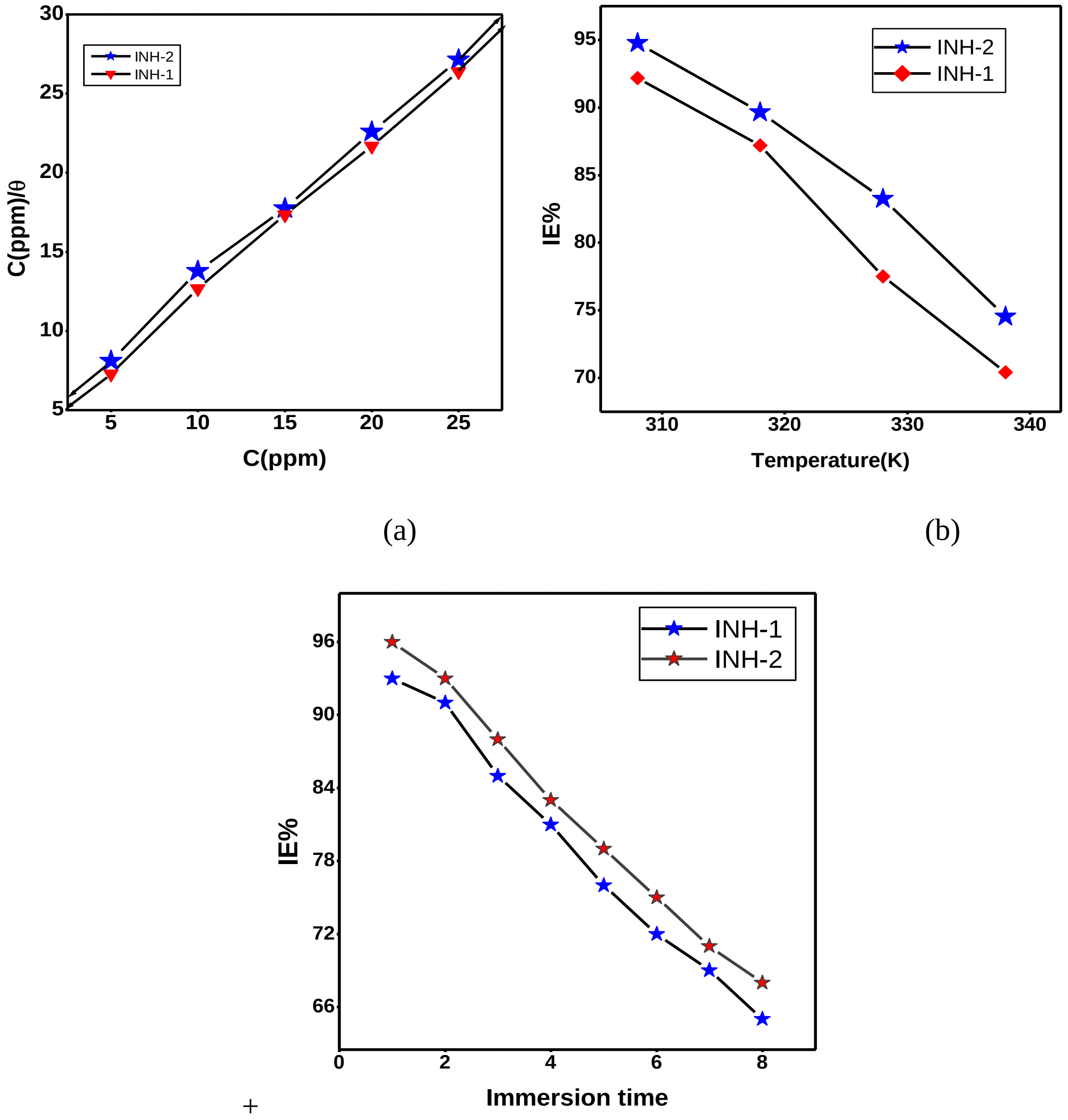
where, $\mathrm{R^{i}_{P}}$ and $\mathrm{R^{0}_{P}}$ and are polarization resistances in inhibited and blank solutions respectively

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

The mild steel coupons were exposed to aerated 1 M HCl for 3 h. It has been found that inhibition efficiency of all the Mannich bases increases with increase in concentration.



(a) (b)

(c)

Figure 2. (a) Inhibition efficiency of inhibitors at different concentrations (b) Inhibition efficiency of inhibitors at different temperatures (c) Inhibition efficiency of inhibitors at different immersion times

The maximum inhibition efficiency for each inhibitor was obtained at 25 ppm concentration and further increase in concentration did not cause any appreciable change in the performance of inhibitors. The variation of inhibition efficiency with increase in inhibitor concentration from 5 ppm to 25 ppm is shown in Figure 2 (a). It is clear that on increasing concentration, inhibition efficiency increases for both the inhibitors. The values of percentage inhibition efficiency (η%) and corrosion rate (C_R) obtained from weight loss method at different concentrations of all the Mannich bases at 308 K are summarized in Table 1.

Table 1. Corrosion rate (C_R) and inhibition efficiency (η%) for mild steel in 1M HCl in absence and in presence of different concentrations of inhibitors from weight loss measurements at 308 K.

Inhibitor	Conc. (ppm)	Weight loss (mg)	Surface coverage (θ)	Inhibition efficiency (η%)	Corrosion rate (mm/y)
Blank	-	230	-	-	85.3
INH-1	5	88	0.617	61.7	32.6
	10	63	0.726	72.6	23.3
	15	36	0.845	84.5	13.3
	20	26	0.886	88.6	9.6
	25	18	0.921	92.1	6.6
INH-2	5	72	0.686	68.6	26.7
	10	53	0.789	78.9	19.6
	15	31	0.865	86.5	11.5
	20	18	0.922	92.2	6.6
	25	12	0.948	94.8	4.4

3.1.2. Effect of Temperature:

In order to study the effect of temperature on the inhibition characteristic of Mannich bases, weight loss measurements were performed at different temperatures from 308 to 338 K in the absence and presence of 25 ppm concentrations of inhibitors for 3 h immersion time. The results are given in Table 2. It is clear that the inhibition efficiency decreased around 30 % at the studied temperature range which indicated desorption of inhibitor molecules to some extent with increasing temperature [16].

3.1.3. Thermodynamic parameters and Adsorption isotherms:

The mechanism of corrosion inhibition may be explained on basis of adsorption behavior [17]. Several adsorption isotherms were tested to describe the adsorption behavior of all the compounds used in study but the Langmuir adsorption isotherm was found to best fit which can be expressed by following equation:

$$\frac{C_{(\mathrm{inh})}}{\theta} = \frac{1}{K_{(\mathrm{ads})}} + C_{(\mathrm{inh})} \qquad (7)$$

where, $C_{(\mathrm{inh})}$ is inhibitor concentration and K_{ads} is equilibrium constant for adsorption-desorption process.

The degree of surface coverage (θ) for different concentrations of inhibitors in 1N HCl at 35-65 ºC for 3 h of immersion time has been evaluated from weight loss values. The data were tested graphically by fitting to various isotherms. The Langmuir and Temkin isotherms were also tested and given in Figure 3(a-b).

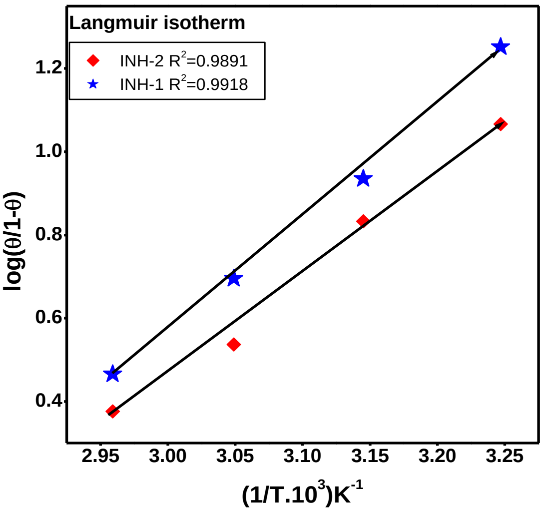


Figure 3. Langmuir adsorption isotherm.

The value of heat of adsorption was determined from the slope ($-\Delta G_{\mathrm{ads}}/2.303RT$) of the graph. The values for heat of adsorption (ΔG_{ads}) were determined by using following equations:

$$\Delta G^{\circ}_{\mathrm{ads}} = -RT\ln(55.5K_{\mathrm{ads}}) \qquad (8)$$

$$\ln K_{\mathrm{ads}} = \frac{-\Delta H^{\circ}_{\mathrm{ads}}}{RT} + \mathrm{constant} \qquad (9)$$

The calculated value of heat of adsorption and adsorption constant are given in Table 2. Since the values of heat of adsorption for the both the Mannich bases are less that -40 KJmol^{-1}, it is suggested that physical adsorption of the inhibitors takes place on the metal surface [18-19].

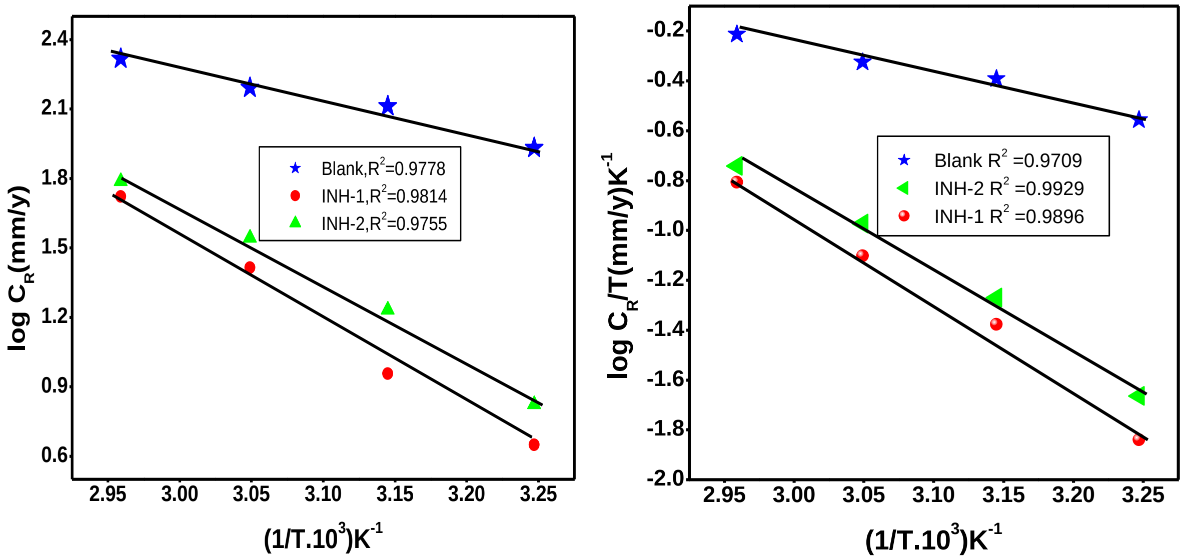
The dependence of corrosion rate at temperature can be expressed by Arrhenius equation and transition state equation:

$$\log(C_{\mathrm{R}}) = \frac{-E_{\mathrm{a}}}{2.303RT} + \log\lambda \qquad (10)$$

$$C_{\mathrm{R}} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^{*}}{R}\right)\exp\left(-\frac{\Delta H^{*}}{RT}\right) \qquad (11)$$

where, E_a apparent activation energy, λ is the pre-exponential factor, ΔH^{*} is the apparent enthalpy of activation, ΔS^{*} the apparent entropy of activation, *h* is Planck's constant and *N* is the

Avogadro number. A linear plot between log(C_R) vs. 1/T and log(C_R/T) vs. 1/T (Figure 4 a-b), with a slope of (-ΔH*/2.303R) and an intercept of [log(R/Nh) + (ΔS*/2.303R)], from which the values of ΔS* and ΔH* were calculated and listed in Table 2. The data shows that thermodynamic activation functions ($E_{\square}$) of the corrosion in mild steel in 1N HCl solution in the presence of the inhibitors is lower than those in free acid solution indicating that all the inhibitors exhibit high inhibition efficiency on increasing the temperature [20]. The negative values of ΔS* indicate that the process of adsorption is spontaneous [21-22].



(a) (b)

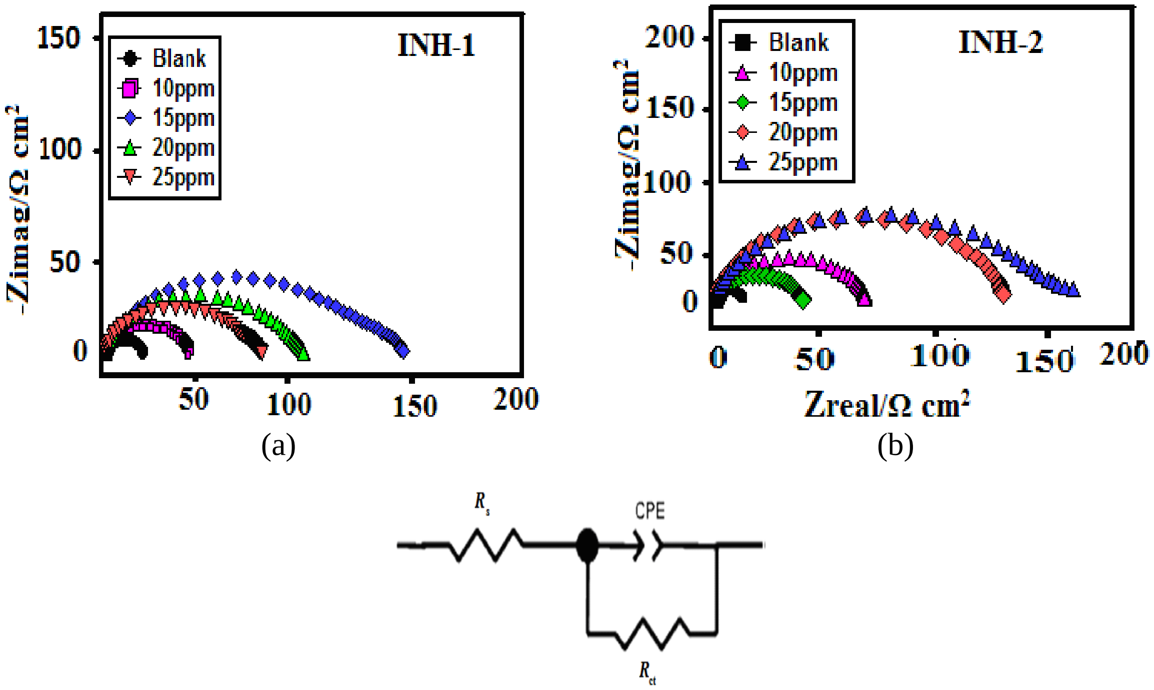
Figure 4. (a) Arrhenius plot of log C_R vs. 1/T (b) Transition state plot of logC_R/T vs. 1/T

Table 2. Thermodynamic parameter for mild steel in 1M HCl in absence and presence of optimum concentration of inhibitors

Inhibitor	Ea (kJ mol^{-1})	-ΔG (kJ mol^{-1})				K_{ads} (M-1 10^3)				ΔH (kJ mol^{-1})	ΔS ($JK^{-1}mol^{-1}$)
		308	318	328	338	308	318	328	338		
Blank	23.48	23.48	-	-	-	-	-	-	-	21.04	-178.9
INH-1	21.27	-34.7	-34.4	-34.2	-34.1	13.99	10.23	7.01	3.46	61.19	-30.16
INH-2	24.41	-35.8	-35.8	-34.9	-34.5	21.45	12.28	8.25	3.88	66.75	-15.09

3.2.1. Electrochemical impedance spectroscopy:

Impedance method provides information about the kinetics of the electrode processes and simultaneously about the surface properties of the investigated systems. The shape of impedance curves gives mechanistic information. Nyquist plots of mild steel in absence and presence of different concentrations of Mannich bases are shown in Fig. 5. And impedance parameters such as R_{ct}, R_s, Y^0, n and C_{dl} calculated from Nyquist plot using equivalent circuit [5 (c)] are given in table.4. From Nyquist plot it is clear that impedance increases with increasing concentration of inhibitors and increase in the inhibition efficiency [23].



(a) (b)

(c)

Figure 5. (a,b) Nyquist plots in absence and presence of different concentrations of inhibitors.(c) Equivalent circuit used to fit the impedance data.

It is clear from the result that the value of R_{ct} increases from 11.8/ Ω cm^2 (Blank) to 147.06/ Ω cm^2 for INH-1 and 155.06/ Ω cm^2 for INH-2 on addition of 25 ppm of inhibitors. The value of C_{dl} decreases from138.2μF cm^{-2} (Blank) to 37.3 μF cm^{-2} for INH-1 and 24.6 μF cm^{-2} for INH-2. The decrease in capacitance (C_{dl}) on addition of inhibitor may be due to increase in local dielectric constant and/or may be due to increase in the thickness of the double layer, showing that both the Mannich bases inhibited Iron metal corrosion by adsorbing at the metal/acid interface [24].

The amplitudes of CPE were calculated by using following equation:

$$Z_{\mathrm{CPE}} = \left(\frac{1}{Y_0}\right)\left[(j\omega)_n\right]^{-1} \qquad (12)$$

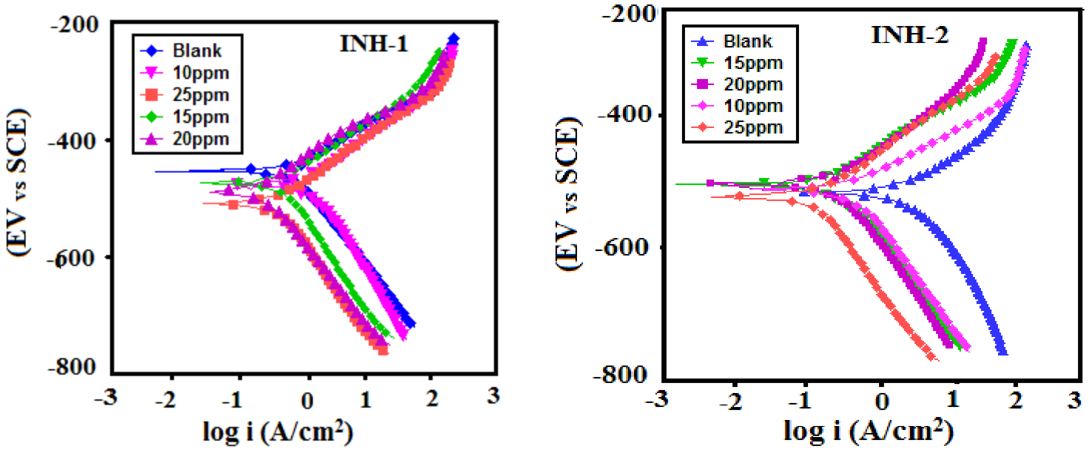
where, Y_0 is magnitude of CPE and j is an imaginary constant. The value of n (phase shift) gives information about degree of inhomogeneities.

Table 3. The Electrochemical Impedance parameters and corresponding efficiencies of the two Mannich bases in 1 M HCl at different concentrations:

Inhibitor	Conc. (ppm)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	Y^0 (μF cm^{-2})	n	C_{dl} μF cm^{-2})	η%
Blank	-	1.11	11.8	249.6	0.827	85.05	-
INH-1	10	1.18	42.94	158.3	0.850	85.0	71.8
	15	0.732	55.68	121.3	0.853	59.3	78.0
	20	0.833	78.65	105.7	0.874	52.2	84.3
	25	1.16	147.06	73.3	0.868	37.3	91.6
INH-2	10	0.735	54.09	149.0	0.870	83.5	77.4
	15	0.879	65.63	107.2	0.873	57.8	81.2
	20	2.30	87.26	97.64	0.855	43.5	85.9
	25	0.987	155.06	56.03	0.838	24.6	92.1

3.3.2. Potentiodynamic polarization measurements:

Polarization curves for mild steel at various concentrations of inhibitors in aerated solutions are shown in Fig. 6a-b. It is clear from the potentiodynamic curves that the presence of inhibitor in acid solution decreases the corrosion rate. The decrease in I_{corr} value is due to the adsorption of the inhibitor molecules [25]. The various electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic slopes (β_a and β_c) were calculated from Tafel plots and corresponding efficiencies are given in Table 4. Addition of the Mannich bases to acid media affected both the cathodic and anodic parts of the curves. Therefore, these compounds behave as mixed-type inhibitors. From the polarization curves it was noted that the curves were shifted toward lower current density region without significant change in corrosion potential and β_c values increased with increase in concentration of inhibitor compounds. The higher β_c values indicated the retardation of cathodic reduction rate.



(a) (b)

Figure 6. (a-b) Tafel polarization curves for corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of Mannich bases.

Table 4. Potentiodynamic polarization parameters and corresponding efficiencies of Mannich bases in 1 M HCl at different concentration:

Inhibitor	Conc. (ppm)	Tafel Polarization					Linear Polarization	
		E_{corr} (mV vs. SCE)	I_{corr} (μA cm^{-2})	β_a (mV/dec)	β_c (mV/dec)	η%	R_P (Ω cm^2)	η%
Blank	-	-445	1160	71.0	114.6	-	11.81	-
INH-1	10	-476	332.5	83.4	148.4	69.8	48.98	73.1
	15	-487	255.3	82.6	170.5	76.8	66.59	80.2
	20	-482	136.5	81.5	121.4	87.6	113.0	88.4
	25	-487	97.8	80.5	107.3	91.2	154.0	91.5
INH-2	10	-487	221.3	78.7	175.0	79.9	69.4	81.03
	15	-473	165.0	74.1	171.0	85.0	105.0	87.46
	20	-488	67.6	69.3	126.7	91.9	135.9	90.31
	25	-486	57.2	65.6	119.6	94.1	304.3	95.2

From results it is clear that addition of inhibitors does not cause any significant shift of E_{corr}. The maximum shift obtained was 22 mV; thus the investigated compounds behave as mixed-type of inhibitors [26-29]: The maximum efficiency were found 91.2% and 94.1% at 25 ppm concentration for INH-1 and INH-2 respectively.

4. MECHANISM OF INHIBITION

The mechanism of corrosion inhibition can be explain on the basis of adsorption mechanism. The investigated inhibitors can adsorbs in 1M HCl on mild steel surface in four ways namely,

(i) Electrostatic interaction between the charged molecules and the charged metal,

$$[\mathrm{INH}] + x\mathrm{H}^{+} \longrightarrow [\mathrm{INH\text{-}H}x]x+$$

(ii) Interaction of unshared electron pairs in the molecule with the metal,

(iii) Interaction of □-electrons with the metal and

(iv) A combination of types (i–iii) [30–32]

Concerning inhibitors, the inhibition efficiency depends on several factors; such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and the formation metallic complexes. The order of efficiency of both the inhibitors is as follows:

INH-2 > INH-1

The higher inhibition efficiency in INH-2 over INH-1 is due to the presence of three additional –OH group in INH-2. It is a well-known fact that the inhibitors not only offer electrons to metal atoms but also have unoccupied higher energy orbital to accept electrons from d-orbital of metal atom for strengthening of bonding interaction [33, 34]. In acid solution mild steel surface bears positive charge;

it is difficult for the protonated molecules to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged Cl^- ions. Thus, there is a synergism between the adsorbed Cl^- ions and protonated inhibitors. Hence, we can assume that the inhibition of mild steel corrosion in 1 M HCl is due to the adsorption of Mannich bases on the mild steel surface.

5. CONCLUSIONS

(1) The above two Mannich bases are good corrosion inhibitors for mild steel corrosion in 1 M HCl solution.

(2) The Potentiodynamic polarization study revealed that both the Mannich bases act as mixed-type inhibitors.

(3) The inhibition efficiency of both inhibitors increases with inhibitor concentration.

(4) The order of inhibition efficiency was as follows INH-2 > INH-1.

(5) The adsorption of Mannich bases on mild steel surface obeys the Langmuir adsorption isotherm.

(6) The highest inhibition efficiency was 91.6 % and 95.6 % at concentration of 25 ppm for INH-1 and INH-2 respectively.

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