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RESEARCH ARTICLE

CORROSION BEHAVIOR OF MILD STEEL IN HYDROCHLORIC ACID SOLUTION IN PRESENCE OF NICOTINIC ACID DERIVATIVES

***Hemapriya, V., Savithri, K., Parameswari, K. and Chitra, S.**

Department of Chemistry, P.S.G.R. Krishnammal College for Women, Coimbatore – 4, Tamil Nadu, India

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ABSTRACT

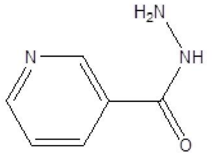
The inhibition effect of the synthesized organic inhibitor namely nicotinic acid hydrazide (NAH) and its benzylidine derivative (NABH) on the corrosion of mild steel in1M hydrochloric acid has been investigated using weight loss, Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization measurements. The inhibition efficiencies obtained from all methods employed are in good agreement with each other. The obtained results show that the compounds NAH and NABH are very good inhibitors with efficiency 90% and 94% respectively at 1.0 mM additive concentration in acid solution. The inhibition efficiency increases with increase of inhibitor concentration. Changes in impedance parameters (R_t and C_{dl}) were indicative of adsorption of the compound on the metal surface, leading to the formation of a protective film. Tafel polarization measurements showed that the inhibitors are mixed type. Adsorption of the inhibitor on the surface of the mild steel in 1M hydrochloric acid was found to obey Langmuir's adsorption isotherm. The activation energy and free energy of adsorption process were calculated and discussed.

INTRODUCTION

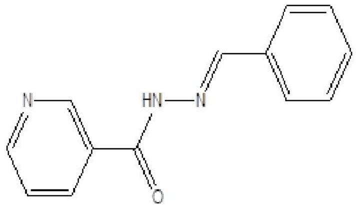
Mild steel is widely applied as construction material in many industries due to its excellent mechanical properties and low cost. Some of the important fields of application being acid pickling, industrial cleaning, oil-well acidizing and petrochemical processes, the main problem of applying mild steel is its dissolution in acidic solutions. The corrosion of mild steel is effectively controlled by the use of suitable inhibitors. The majority of the well known inhibitors are compounds containing N, O, P and S in their functional groups with aromatic and heterocyclic rings. The inhibitors are adsorbed on the metal surface and provide a barrier between metal and environment thereby reducing the rate of corrosion. The objective of the present study was to evaluate the anticorrosive performance of nicotinic acid hydrazide (NAH) and its benzylidene derivative (NABH) on mild steel in acid medium.

MATERIALS AND METHODS

Mild steel specimens having dimension of 3 cm X1 cm X 0.05 cm (C=0.079%, P=0.025%, Mn=0.018%, S=0.021%, Rest: Fe) were used for the weight loss measurement. nicotinic acid hydrazide (NAH) and its benzylidene hydrazide (NABH) were synthesized from nicotinamide by reported procedure (Jaya preethi *et al*., 2012).



Nicotinic acid hydrazide



Nicotinic acid benzylidene hydrazine

Weight loss method

The mild steel specimens were polished using emery sheets of various grades and degreased with trichloroethylene. The polished specimens were weighed and immersed in 1M HCl with various concentrations of the inhibitors and without

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**Corresponding author: Hemapriya, V.,*
Department of Chemistry, P.S.G.R. Krishnammal College for Women, Coimbatore – 4, Tamil Nadu, India

inhibitor. After three hours, the specimen were taken out, washed with running water, dried and weighed. From the initial and final weights of the specimen, weight loss was calculated. From the weight loss data the inhibition efficiency, corrosion rate and the surface coverage were calculated. To know the effect of temperature, the above procedure was followed at different temperatures (303K, 313 K, 323 K and 333 K) for optimum concentration (1mM) of the inhibitors.

Electro chemical studies

The electrochemical measurements were carried out in a glass cell with a capacity of 100ml. A platinum electrode and saturated calomel electrode were used as counter electrode and reference electrode respectively. The mild steel electrode in the form of cylindrical rod embedded in Teflon with an exposed area 0.785cm^2 was then placed in the test solution (uninhibited and inhibited solution) for 10- 15 minutes before electrochemical measurements. The Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit, Ivium Compactstat. The EIS measurement was made at a corrosion potential over a frequency range 0.01Hz to 10000Hz with a signal amplitude of 25mV. The Tafel polarization were made after EIS for a potential range of -200mV to + 200 mV with respect to open circuit potential, at a scan rate of 1mV/sec. From Nysquist plot (Z real Vs Z imaginary) electrochemical resistance (Rt) and double layer capacitance (C_{dl}) were calculated. From the plot of potential, E Vs log I, the corrosion potential (Ecorr), corrosion current, (Icorr) and Tafel slopes for the cathodic and anodic reaction (bc, ba) were obtained.

Synergistic effect of halide ions

The synergistic effect was studied by the addition of 1mM KI to the mild steel specimen immersed in 1M HCl containing various concentrations of the inhibitors for a duration of three hours. From the weight loss data, the corrosion rate and inhibition efficiency were calculated. The same procedure was repeated by the addition of 1mM KCl and 1mM KBr.

RESULTS AND DISCUSSION

Weight Loss Method

The inhibition efficiency of the inhibitors (NAH & NABH) at various concentrations for mild steel corrosion in 1M HCl has been evaluated by weight loss measurements and the results are summarized in Table 1.

The data revel that inhibition efficiency increases with increase in concentration of the inhibitors whereas corrosion rate decreases with increase in inhibitor concentration. The decrease in corrosion rate (or) increase in inhibition efficiency with concentration may be due to the adsorption of inhibitors on the metal surface making a barrier film for mass and charge transfer thus protecting the metal surface from corrosion. The degree of protection increases with increase in surface fraction occupied by the adsorbed inhibitor molecules.

Table 1. Inhibition efficiency of the compounds for mild steel corrosion in IM HCl obtained from weight loss measurements

Name of the inhibitor	Inhibitor concentration (mM)	Weight loss(gms)	Inhibitor efficiency (%)	Corrosion rate (mpy)	Degree of coverage (θ)
NAH	Blank	0.1158		36893.88	
	0.2	0.0372	67.87	11851.92	0.6787
	0.4	0.0262	77.37	8347.32	0.7737
	0.6	0.0173	85.06	5311.78	0.8506
	0.8	0.0164	85.83	5225.09	0.8583
	1.0	0.0106	90.84	3377.16	0.9084
NABH	0.2	0.0331	71.41	10545.66	0.7141
	0.4	0.0196	83.07	6244.56	0.8307
	0.6	0.0098	91.53	3122.28	0.9153
	0.8	0.0089	92.31	2835.54	0.9231
	1.0	0.0062	94.64	1975.32	0.9464

Effect of temperature

The temperature performance (303 – 333 K) of the compounds at the best inhibitor concentration of 1.0 mM for the corrosion inhibition of mild steel in IM HCl are given in Table 2 and the corresponding Arrhenius plots are depicted in Figure 1. It can be seen from the table that inhibitor efficiency decreased with increase in temperature.

Table 2. Inhibition efficiency of inhibitors at 1.0mM concentration for mild steel corrosion obtained by weight loss measurements at various temperatures in IM HCl

Name of the inhibitor	Temperature (k)	Weight loss (gms)	Inhibition efficiency (%)	Corrosion rate (mpy)
NAH	303	0.0031	75.00	2962.05
	313	0.0095	58.33	9077.25
	323	0.0178	53.15	17007.9
	333	0.0534	12.74	51023.7
NABH	303	0.0018	85.48	1719.9
	313	0.0098	57.01	9363.9
	323	0.026	31.57	24843
	333	0.0533	12.90	50928.15

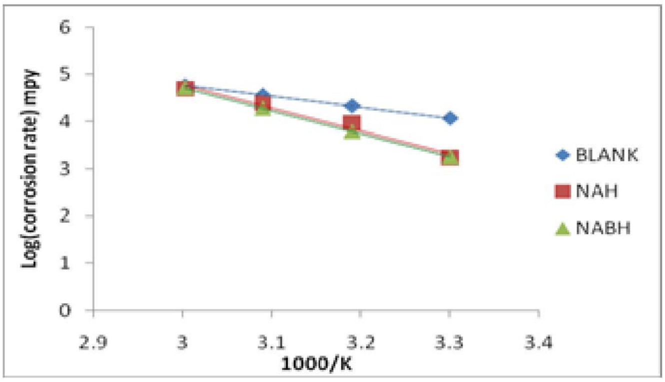

Fig 1. Arrhenius plot of corrosion rate of mild steel in IM HCl in presence and absence of the inhibitors

Table 3. The free energy of adsorption and activation energy of inhibitors at various temperature and activation energy of the inhibitors

S.No	Name of the Inhibitor	Ea (kj)	ΔG^{o}_{ads} AT VARIOUS TEMPERATURES (KJ)			
			303 K	313 K	323 K	333 K
1	Blank	47.96	-	-	-	-
2	NAH	96.75	-12.88	-11.32	-11.12	-5.79
3	NABH	101.46	-14.38	-11.14	-10.47	-5.40

This may be due to the fact the inhibitive film formed on the metal surface was less protective in nature at higher temperatures because of desorption of the inhibitor molecules from the metal surface. Like most chemical reaction, the corrosion of mild steel in aqueous acid solution increases with increase in temperature. The diminished effectiveness of the tested inhibitors under the influence of increasing temperature may be attributed to diminished coverage by the inhibitor. This is based on the assumption that metal dissolution occurs on that part of the surface, free of adsorbed molecules (Abdel-Aal *et al*., 2001). The activation energy, Ea, was calculated from the slopes of Arrhenius plots for uninhibited and inhibited systems. It is apparent from the values of Ea (Table 3) that the activation energy is higher in the presence of inhibitor. The adsorption of inhibitor molecule causes an increase in the activation energy of the process. This is because the organic compounds have reaction centers that can block the active sites for corrosion resulting in an increase in activation energy (Sathya *et al*., 2009).

Adsorption isotherm

Basic information on the interaction between the inhibitor and the alloy surface can be provided by adsorption isotherm. To obtain the isotherm, the fractional coverage values θ as a function of inhibitor concentration were calculated from the weight loss method. Attempts were made to fit the θ values to various isotherms Langmuir isotherm provided the best fit for the adsorption of the studied inhibitors. Fig 2 shows the plot of C_{inh} / θ Vs C_{inh} and the expected linear relationship is obtained. The value of regression coefficient (R^2) confirmed the validity of the approach. The slope of the straight line is 0.997 suggesting that the inhibitor form a monolayer on the steel surface and there is no interaction between the adsorbed inhibitor molecules (Arrok *et al*., 2013). The equilibrium constant of adsorption is related to the standard free energy of adsorption (ΔG^{o}_{ads}) by the equation

$$K_{ads} = \frac{1}{55.5} \exp \frac{-\Delta G^{o}_{ads}}{RT}$$

Where 55.5 is the concentration of water in mol/lit in the solution (Olivares *et al*., 2006). The negative value of ΔG^{o}_{ads} and the higher value of K_{ads} reveal the spontaneity of the adsorption process and the stability of adsorbed layer on the mild steel surface. Generally ΔG^{o}_{ads} values of -20KJ/mol or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physisorption). Those of -40KJ or more involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate bond (chemical adsorption) (Abiola *et al*., 2004). The calculated ΔG^{o}_{ads} values are less than -20KJ/mol showing that the inhibitors chosen for the study are physisorbed on the metal surface.

Electrochemical studies

Polarization studies

The typical Tafel polarization plots of mild steel in 1M HCl in the presence and absence of NAH at different concentrations are shown in Fig 3. The various corrosion kinetic parameters obtained from the Tafel plots are given in Table 4.

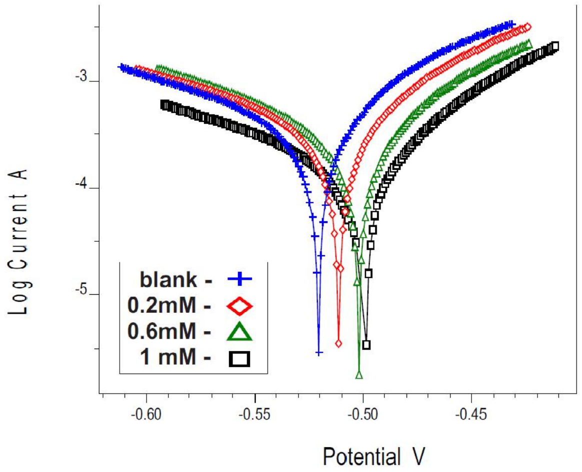

Fig. 3. Tafel plots for mild steel in IM HCl in presence and absence of NAH

Table 4. Corrosion kinetic parameters for mild steel at selected concentration of the inhibitors in IM HCl by potentiodynamic polarization method at 30 ± 1°C

Name of the inhibitor	Inhibitor concentration (mM)	Tafel slopes (mV/decade)		E_{corr} (mV)	I_{corr} ($\mu A/Cm^2$)	Inhibition efficiency (%)
		b_c	b_a			
	Blank	129	80	-525.5	1204	
NAH	0.2	134	78	-512.6	945	21.51
	0.6	116	72	-501.8	831.7	30.92
	1.0	136	66	-499.5	474.2	60.61
	0.2	108	64	-517.5	499.4	58.52
NABH	0.6	127	71	-499.4	496	58.80
	1.0	109	67	-496	439	63.53

The Inhibitor efficiency (%) is calculated using the equation,

$$\text{I.E\%} = \frac{I_{\text{(corr) blank}} - I_{\text{corr (inh)}}}{I_{\text{(corr) blank}}}$$

The data in Table 4 show that increasing NAH concentration slightly shifts the values of the corrosion potentials (E_{corr}) in the less negative direction indicating that the inhibitor acts as mixed type reducing anodic dissolution also retarding the cathodic hydrogen evolution reaction. The cathodic and Anodic Tafel slopes ba & b_c are both affected in the presence of inhibitors confirming their mixed type.

EIS Studies

The effect of the inhibitor (NAH) concentration on the impedance behavior of mild steel in 1M HCl solution has been studied. The Nyquist plots are given in Fig 4.

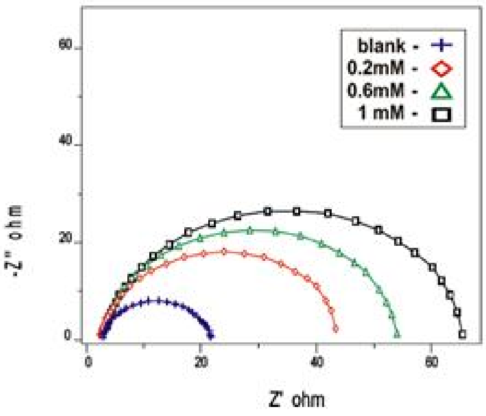

Fig. 4. Nyquist diagram for mild steel in IM HCl in presence and absence of NAH

The Nyquist plots are semicircular showing that the corrosion of mild steel in 1MHCL is mainly controlled by charge transfer process (Chetouani *et al*., 1978). According to Tsuru *et al.* (1978) the charge transfer resistance R_t must correspond to the resistance between the metal and the outer Helmholtz plane and can be calculated from the difference in impedance at lower and higher frequency. The double layer capacitance C_{dl} is obtained from the frequency at which the imaginary component of the impedance (Z^{11}) is maximum. The impedance results are given in Table 5.

Table 5. AC impedance parameters for mild steel at selected for mild steel at selected concentrations of the inhibitors in IM HCl

Name of the inhibitor	Inhibitor concentration (mM)	R_t (ohm/cm^2)	Inhibition efficiency (%)	C_{dl} (µF/Cm^2)
	BLANK	20.5		76.1
NAH	0.2	34.6	40.75	53.9
	0.6	39.72	48.38	51.9
	1.0	47.68	57.00	47.1
NABH	0.2	35.18	41.72	58.9
	0.6	43.03	52.35	43.4
	1.0	55.78	63.24	42.3

It is evident that the impedance response changes significantly. With increasing concentration of inhibitor R_t values increase and C_{dl} values decrease. This may be attributed to the adsorption of inhibitor on the steel surface forming a barrier film which decreases the dissolution of steel in acid medium.

Synergistic effect of halide ions

The synergistic effect provided by the addition of halide ions such as I^-, Br^- and Cl^- to the solution containing 1M HCl and the inhibitors was studied by weight loss method and the data are presented in Table 6. Analysis of the data reveals that the addition of halides to the inhibitors increases the inhibition at each concentration of the inhibitor tested. This increase in inhibition efficiency shows that the mechanism of the synergistic action is due to the co-adsorption of halides and the inhibitor. The strong chemisorptions of halide ions on mild steel surface make the iron surface negatively charged one. Organic compounds containing nitrogen in aqueous acid solutions may exist either as neutral molecules or cations. The positively charged protonated cations may then be adsorbed by coulombic attraction on the metal surface where halide ions are already adsorbed. This leads to more surface coverage and hence greater inhibition. The order of synergism of halide ions with tested inhibitors has been found to be $I^- > Br^- > Cl^-$. The reason for better synergism with iodide ion is due to the large size and ease of polarisability of I^- ion, which facilitated chemisorptions on the iron surface.

Table 6. Synergistic effect of 1mM KCl/KBr/KI on the inhibition efficiency of inhibitors in 1M HCl by weight loss method

S.NO	Name of the inhibitor	Inhibitor concentration (mM)	Inhibition efficiency (%)			
			without KCl/KBr/KI	With 1(mM) KCl	With 1(mM) KBr	With 1(mM) KI
1	NAH	0.01	51.42	53.94	56.78	58.27
		0.05	54.31	56.97	59.33	61.36
		0.10	62.98	65.92	66.45	69.89
		0.15	66.22	68.35	70.46	72.75
		0.2	67.87	70.79	71.47	73.50
2	NABH	0.01	55.31	57.45	61.73	64.85
		0.05	56.27	59.97	62.76	66.57
		0.10	66.88	68.18	71.09	74.00
		0.15	69.52	71.35	74.32	77.49
		0.2	71.41	73.70	76.35	78.64

Effect of structure

A comparison of the inhibition efficiency of the two inhibitors studied shows that NABH shows greater efficiency than NAH. The inhibition efficiency of an additive depends on many factors like number of adsorption active centers in the molecule, their charge density, molecular size, mode of adsorption, heat of hydrogenation and formation of metallic complexes. NABH contains a CH=N group and an additional phenyl ring in conjugation with it. Planarity of the π electron cloud and lone pair of electrons present on the nitrogen atoms are the important features that determine the adsorption of NABH molecules on mild steel. The N atom in CH=N group is in sp^2 hybridised state and has one π molecular orbital and p_z atomic orbital can interact with π molecular orbital of the C atom in the benzene ring to form p-π conjugation (Iran Sheikhshoaie *et al*., 2009). Because of this the π electron can be easily translated to the d-orbital of the metal atoms on mild steel surface. Hence adsorption and inhibition are enhanced in the case of NABH which shows > 95% efficiency.

Conclusion

The main conclusions drawn from this study are NAH and NABH inhibit the corrosion of mild steel in 1M HCl medium. The inhibitors behave as mixed type. Adsorption of inhibitors on the surface of mild steel in 1M HCl obeys Langmuir's adsorption isotherm. Reduction in the values of I_{corr} and C_{dl} in the presence of an inhibitor shows the formation of barrier film. The inhibition efficiency of the inhibitors increases with increase in inhibitor concentration and decreases with increase in temperature.

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