Research Article

(E)-3-[thiophen-2-ylmethyleneamino]benzoic Acid: Structural and Corrosion Inhibition Studies

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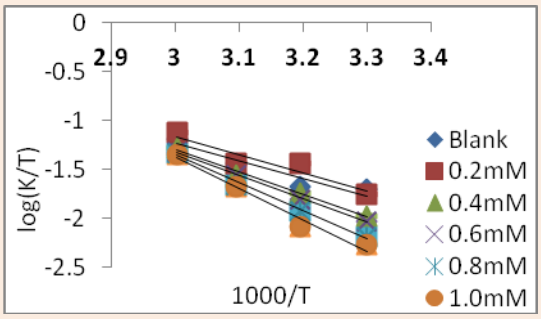
Abstract

A novel Schiff base, (E)-3-[thiophen-2-ylmethyleneamino]benzoic acid (T2YMABA) was synthesized from thiophene-2-carbaldehyde and 3-aminobenzoic acid. Structure of the ligand was derived on the basis of various analytical techniques such as ^{1}Hnmr, ^{13}Cnmr, infrared, mass and electronic spectroscopy. The corrosion inhibition efficiency of the Schiff base T2YMABA on mild steel in 1.0M HCl and 0.5M H_2SO_4 media has been investigated and compared using conventional weight loss measurements at different concentrations and adsorption studies. The Schiff base exhibited corrosion inhibition on mild steel in HCl medium and the inhibition efficiency increased with the increase in concentration of the inhibitor. Corrosion inhibition behaviour at elevated temperatures was also conducted. The adsorption of the inhibitor on the surface of the corroding metal obeys Langmuir isotherm in HCl medium and Freundlich isotherm in H_2SO_4 medium. Thermodynamic parameters (K_{ads}, ΔG^0_{ads}) were also calculated. The results showed that the inhibitor T2YMABA possesses greater inhibition effect towards mild steel in 1.0M HCl medium.



Keywords: Schiff base, corrosion inhibitors, isotherm

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Introduction

The use of corrosion inhibitors is one of the most effective methods to protect metal surfaces against corrosion, especially in acid media [1-4]. Recently the development of corrosion inhibitors is based on organic compounds which perform this role well and new series are developing to replace the inorganic ones. The adsorption properties of organic molecules are responsible for their corrosion inhibition efficiency. Molecules containing nitrogen, oxygen, sulphur atoms and multiple bonds facilitate adsorption on the metal surface [5]. It is reported that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule which is related to its functional groups, possible sterric effects and electronic density of donor atoms [6-10]. Now-a-days the availability of sophisticated computational tools and electrochemical techniques provide a better understanding of corrosion inhibitors and their mechanisms [11]. In the present course of investigation, a novel potential Schiff base (E)-3-(thiophen-2-ylmethyleneamino)benzoic acid (T2YMABA) was synthesized from thiophene-2-carbaldehyde and 3-aminobenzoic acid, and characterized using various analytical tools and physicochemical studies. The corrosion inhibition efficiencies of the Schiff base were compared on mild steel in 1M HCl and 0.5M H_2SO_4 solutions using gravimetric methods and adsorption studies.

Experimental

Synthesis of the Schiff base

The heterocyclic Schiff base T2YMABA was synthesized by the condensation of equimolar mixture of thiophene-2-carbaldehyde and 3-aminobenzoic acid in ethanol medium. The reaction mixture was refluxed for 3 hours, concentrated and cooled. The precipitated ligand was filtered, washed with dil. alcohol (1:1) and dried over P_2O_5.

The aggressive solutions of 1M HCl and 0.5M H_2SO_4 were prepared by dilution of A.R grade (Merck) 37% of HCl and 98% H_2SO_4 with de-ionized water. Inhibitor solutions were prepared in the range 0.1mM-1mM concentrations.

Gravimetric studies on corrosion inhibition

The weight loss experiments were carried out under total immersion conditions in test solution maintained at 300K. Mild steel specimens of 1.5x 2x 0.1 cm dimension were cut and abraded with various grades of silicon carbide papers (200, 400, 600, 800, 1000, 1200 and 2000). The exact area and thickness of each coupon were measured and washed. Specimens were then degreased with acetone and finally dried. After weighing, specimens were separately immersed in 50ml 1M HCl and 0.5M H_2SO_4 solutions in the absence and presence of the Schiff base T2YMABA. Weight loss of metal specimens was noted at every 24 h time interval for five days. The experiments were carried out in duplicate and the average values were reported. The corrosion rate (ν) is calculated by the following equation

$$\nu = \frac{W}{St} \quad (1)$$

where, W is the average weight loss of coupon, S is the total area of specimen, t is the time of treatment [12]. The percentage of inhibition efficiency (η) can be calculated by the following equation

$$\eta_w\ \% = \frac{\nu_0 - \nu}{\nu_0} X100 \quad (2)$$

where, ν_0 and ν are the corrosion rates of uninhibited and inhibited specimens respectively [13].

Results and discussions

Characterization of the Schiff base

The ^{1}H NMR spectrum of the Schiff base exhibited nine characteristic peaks due to nine different types of protons present in it. A broad peak of singlet nature at 12.93δ can be assigned to the carboxylic acid proton. Signals obtained in the range 7.16--8.79 δ are due to different aromatic protons of both thiophene and benzenoid rings. The ^{13}C NMR spectrum of the ligand exhibited twelve distinct peaks corresponding to12 carbon atoms in different chemical environment in the molecule. The carboxylate carbon of the Schiff base gave its characteristic signal at 167.03ppm. The azomethine carbon exhibited sharp peak at 154.99ppm. Ten non equivalent carbon atoms on aromatic rings showed their typical peaks between 121.34-150.94ppm. Table 1 gives the ^{1}H NMR and ^{13}C NMR data of the Schiff base.

Table 1 ^{1}H Nmr and ^{13}C NMR spectral data of the ligand T2YMABA

^{1}HNMR spectral data of the ligand T2YMABA (δ values)	12.93, 8.79, 7.78, 7.73, 7.70, 7.66, 7.44, 7.16, 3.25
^{13}CNMR spectral data of the ligand T2YMABA (δ values)	167.03, 154.99, 150.94, 142.19, 134.19, 131.95, 131.57,129.54, 128.29, 126.70, 125.77, 121.34

The appearance of only one peak in the gas chromatogram ascertains the purity of the sample. The molecular ion peak in the mass spectrum of the Schiff base T2YMABA appeared at m/z value 231, which is in excellent agreement with the molecular weight of the compound. The other significant peaks exhibited in the spectrum can be explained by the usual fragmentation pattern of carboxylic acids and imines.

In the IR spectrum, a peak observed at 3000cm^{-1} is the scalloped band of OH group of the carboxylic acid functional group. The characteristic peak of C-H of the aromatic ring is overlapped with the above band. The peak at 2872cm^{-1} is due to the C- H of the azomethine group. A strong band at 1689 cm^{-1} is attributed to the symmetric stretching of C=O of carboxylic acid. A strong peak at 1579 cm^{-1} can be assigned to the stretching frequency of azomethine(C=N) group. A sharp peak at 1415 cm^{-1} is due to the bending vibration of the C-H bond. The bending vibrations of C-Hof aromatic group are observed at 914 cm^{-1} and 717 cm^{-1}.

The characteristic bands due to n→π* and π → π* transitions are exhibited by the ligand in its electronic spectrum at 32154 $cm^{-1}$and 39062cm^{-1} respectively. The spectral studies listed above and the CHN data. (C,62.48; H,4.67; N,4.88; S,27.92 %) suggest the following structure for the Schiff base T2YMABA (Figure 1).

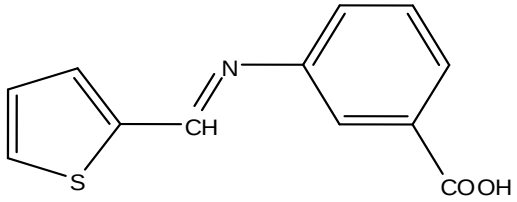

Figure 1 Molecular Structure of T2YMABA

Weight loss measurements

The variation of corrosion rate and inhibition efficiency with immersion time was determined by weight loss measurements for a period of five days in the presence and absence of T2YMABA. From Table 2 it is clear that the rates of corrosion of the MS specimens decrease with increase in concentration of the T2YMABA while the percentage of inhibition is markedly increased with increase in concentration which can be attributed to the increased adsorption of the T2YMABA molecules on the metal surface [14]. The increased surface coverage may partially hinder the reaction between metal and H^+ ions which in turn increase the percentage of inhibition. The inhibition efficiency showed a saturation value 72.99% and 45.89% at the inhibitor concentration 1.0mM in 1.0MHCl and 0.5M H_2SO_4 medium respectively.

Table 2 The corrosion rate and percentage of inhibition efficiencies of T2YMABA for MS specimens immersed in 1.0M HCl and 0.5M H_2SO_4 for 24 h

Conc. (mM)	1.0M HCl		0.5M H_2SO_4	
	ν (mmy^{-1})	η_w%	ν (mmy^{-1})	η_w%
0	5.93	-	26.11	
0.2	5.32	25.32	24.97	4.35
0.4	3.19	46.08	22.09	15.39
0.6	2.79	52.90	20.67	20.84
0.8	1.95	67.17	16.05	38.53
1.0	1.60	72.99	14.13	45.89

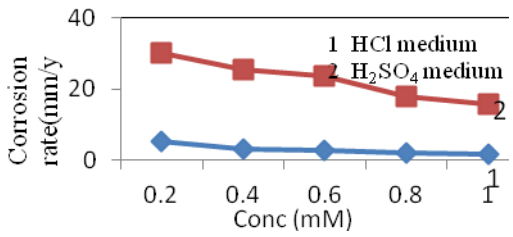

Figure 2 The variation of corrosion rate in presence of the inhibitor T2YMABA at different concentrations at 30^0C

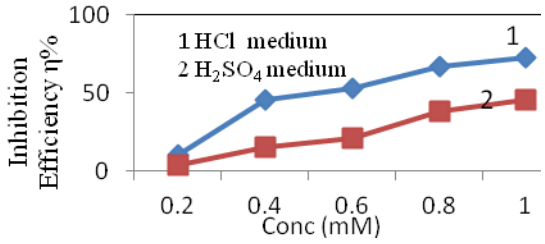

Figure 3 The variation of inhibition efficiency in presence of the inhibitor T2YMABA at different concentrations at 30^0C

Effect of temperature in 1.0M HCl medium

The effect of temperature on corrosion rate was also evaluated using weight loss measurement in the temperature range of 30-60 ^{0}C. The activation energy of corrosion with and without the inhibitor could be calculated by Arrhenius equation

$$K = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where, K is the rate of corrosion, E_a the activation energy, A the frequency factor, T the temperature in Kelvin scale and R is the gas constant. A plot of log (K/T) Vs 1000/T in the presence and absence of the inhibitor is represented in Figure 4. Figure 5 gives the linear plots between log K and 1000/T having regression coefficients close to unity which indicate that the corrosion of MS in HCl could be explained by the simple kinetic model. Enthalpy and entropy of activation (ΔH*, ΔS*) were calculated from the transition state theory

$$K = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (4)$$

where, N is the Avogadro number and h is the Planks constant. Table 3 gives the activation energy and thermodynamic parameters of corrosion. The increase of activation energy of dissolution of the metal with increase in the inhibitor concentration implies the increase in the reluctance of dissolution of metal. Positive signs of enthalpies with a regular rise reflect the endothermic nature of dissolution and the increasing difficulty of corrosion with the inhibitor. The entropy of activation also increases with the inhibitor concentration. For the lower concentrations of the inhibitor, the entropy of activation is negative indicating that the activated molecules are in highly ordered state than that at the initial state. But as the concentration of inhibitor rises, the disordering of activated complex becomes more significant and the entropy of activation becomes positive.

Table 3 Thermodynamic parameters of corrosion of MS in 1.0M HCl with and without the inhibitor T2YMABA

C (mM)	E_a (kJ mol^{-1})	A	ΔH*(kJ mol^{-1})	ΔS*(J mol^{-1} K^{-1})
Blank	37.21	1.3X10^7	37.2	-61.33
0.2	36.56	9.2X10^7	36.6	-64.22
0.4	46.64	3.4X10^8	46.6	-34.16
0.6	48.83	7.1X10^8	48.8	-28.09
0.8	57.57	1.5X10^{10}	57.6	-02.47
1.0	64.39	1.7x10^{11}	64.4	17.64

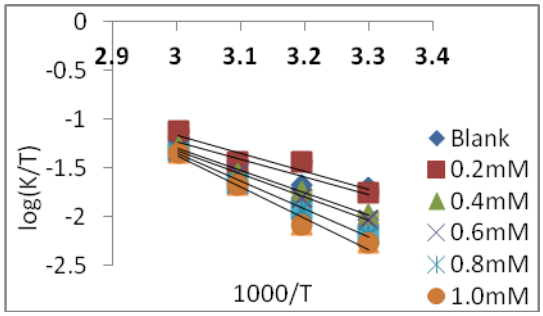

Figure 4 Plots of log (K/T) Vs 1000/T

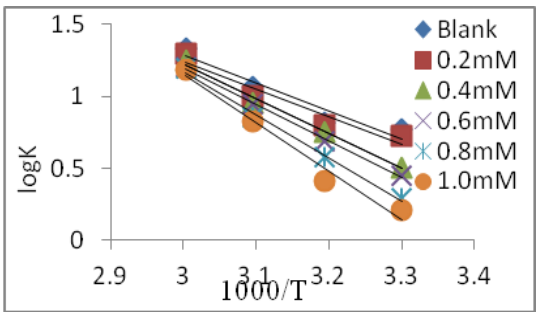

Figure 5 Arrhenius plots to calculate the activation energy

Comparison of inhibition efficiency of Schiff base with its parent amine

To compare the inhibition efficiencies of Schiff base and parent amine, 3-aminobenzoic acid (ABA), weight loss measurements of MS specimens were performed in both 1.0M HCl and 0.5M H_2SO_4 media and the data are represented in Table 4. The inhibition efficiency of the Schiff base T2YMABA was markedly higher than that of the parent amine, for the studied concentrations. This investigation clearly established the role of azomethine linkage (C=N) present in the Schiff base which actively participate in the corrosion inhibition mechanism.

Table 4 The percentage of inhibition efficiencies of ABA and T2YMABA for MS specimens immersed in 1.0M HCl and 0.5M H_2SO_4 for 24 h

Conc. (mM)	η_w% in 1.0M HCl		η_w% in 0.5M H_2SO_4	
	ABA	T2YMABA	ABA	T2YMABA
0.2	4.29	25.32	4.14	4.35
0.6	29.13	52.90	10.83	20.84
1.0	38.42	72.99	21.35	45.89

Adsorption isotherm and free energy of adsorption

The mechanism of adsorption and the surface behaviour of organic molecules can be easily viewed through adsorption isotherms. Different models of adsorption isotherms considered are Langmiur, Temkin, Frumkin and Freundlich isotherms. For the evaluation of thermodynamic parameters it is necessary to determine the best fit isotherm with the aid of correlation coefficient (R^2). Among the isotherms mentioned above, the best description of the adsorption behaviour of T2YMABA on MS specimens in 1M HCl is Langmiur adsorption isotherm which can be expressed as

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

Where, C is the concentration of the inhibitor, θ is the fractional surface coverage and K_{ads} is the adsorption equilibrium constant [15]. Fig. 6 represents the Langmiur adsorption plot of T2YMABA in HCl medium obtained by the weight loss measurements.

In Sulphuric acid medium, the best fit isotherm is Freundlich which can be represented as

$$\theta = K_{ads} C \quad (6)$$

Where, C is the concentration of the inhibitor, θ is the fractional surface coverage and K_{ads} is the adsorption equilibrium constant [16]. Figure 7 represents the Freundlich adsorption isotherm for T2YMABA. The adsorption equilibrium constant K_{ads} is related to the standard free energy of adsorption ΔG^0_{ads}, by

$$\Delta G^0_{ads} = -RT\ln(55.5\ K_{ads}) \quad (7)$$

where 55.5 is the molar concentration of water, R is the universal gas constant and T is the temperature in Kelvin [17]. The negative value of free energy of adsorption indicates the spontaneity of the process. In the present investigation T2YMABA molecules showed ΔG^0_{ads}values as -28.72 kJ/mol and -25.75 kJ/mol in HCl and H_2SO_4 media suggesting that the adsorption involves physisorption in both cases [18].

Table 5 Thermodynamic parameters K_{ads} and ΔG^0_{ads}derived from adsorption isotherms

Medium	Isotherm	K_{ads}	ΔG^0_{ads}(kJ mol^{-1})
1.0M HCl	Langmuir	1600	-28.72
0.5M H_2SO_4	Freundlich	531	-25.75

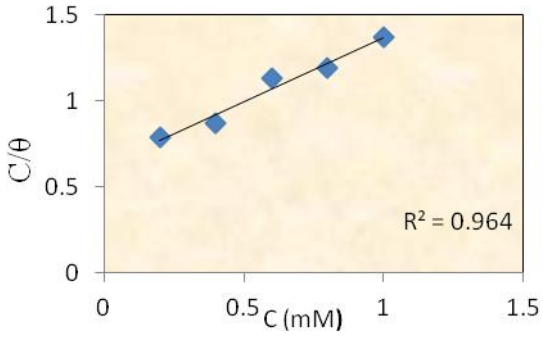

Figure 6 Langmiur isotherm for T2YMABA in 1.0M HCl for 24 h

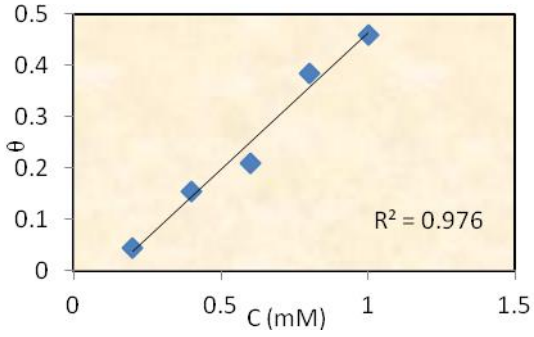

Figure 7 Freundlich isotherm for T2YMABAin 0.5M H_2SO_4 for 24 h

Conclusions

The relative inhibition efficiencies of Schiff base were studied in 1.0M HCl and 0.5M H_2SO_4 solutions. The inhibitor showed a higher inhibitive efficiency for mild steel in 1M hydrochloric acid. The percentage inhibitive efficiency increases with increase in concentration. It is believed that in HCl medium, the Cl^- ions are specifically adsorbed on the metal surface and creates an excess of negative charge on the surface which will favour the adsorption of protonated Schiff base on the surface and hence reduce the dissolution of Fe to Fe^{2+}. Besides this electrostatic interaction between the protonated Schiff base and the metal surface, interactions of unshared electron pairs in the molecule with the metal or the interaction of π-electrons with the metal or a combination of the two are possible [19]. The π-electron cloud of the aromatic rings and the azomethine linkage also participate in the inhibition mechanism. Furthermore, the double bonds in the inhibitor molecule permit the back donation of metal d electrons to the π* orbital and this type of interaction cannot occur with amines [20]. This can be justified by the lower inhibition efficiency of the parent amine than that of Schiff base. Free energy calculations revealed that T2YMABA molecules are adsorbed on the metal surface through physisorption in both media. The Schiff base obeys Langmiur adsorption isotherm in HCl medium and Freundlich isotherm in H_2SO_4 medium. From the above observations it is concluded that the inhibitor T2YMABA exhibits a better corrosion inhibition performance in HCl medium than in H_2SO_4 medium.

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