N-(Piperidinomethyl)-3-[(pyridylidene)amino]isatin: A new and effective acid corrosion inhibitor for mild steel

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ABSTRACT

A new corrosion inhibitor namely N-(piperidinomethyl)-3-[(pyridylidene)amino]isatin (PPI) has been synthesized and its influence on corrosion inhibition of mild steel in 1N hydrochloric acid solution has been studied by weight loss and potentiodynamic polarisation techniques. The inhibitor (PPI) showed more than 94% inhibition efficiency (IE) and an optimum concentration of 300 ppm. The inhibition efficiency of inhibitor has been found to vary with inhibitor concentration, solution temperature, immersion time and acid concentration. Various parameters (E_a, ΔG_{ads}, Q, ΔH, ΔS) for adsorption reveal a strong interaction between inhibitor and mild steel surface. The negative values of G_{ads} indicate the spontaneous adsorption of the inhibitor on mild steel surface. Potentiodynamic polarisation studies show that PPI is a mixed type inhibitor. It inhibits mild steel corrosion by blocking the active sites of metal. Electrochemical impedance spectroscopic (EIS) techniques were also used to investigate the mechanism of corrosion inhibition.

1. Introduction

A study of organic corrosion inhibitors in acid medium is an attractive field of research due to its industrial usefulness [1,2]. A perusal of literature [3,4] reveals that most of the commercial inhibitor formulations include carbonyls and amines as essential ingredients. It has been observed that condensation products of carbonyls and amines, which are known as anils or Schiff's bases, give higher inhibition efficiency than that for constituent carbonyls and amines [5–8]. The condensation products of an amine with an active hydrogen and a carbonyl compound having active hydrogen adjacent to carbonyl with formaldehyde, which are known as Mannich bases. A few Mannich bases have been reported effective acidizing corrosion inhibitors [9,10] and vapour phase corrosion inhibitors [11]. In view of high performance of Mannich bases as corrosion inhibitors we have synthesized a new Mannich base corrosion inhibitor namely, N-(piperidinomethyl)-3-[(pyridylidene)amino]isatin (PPI) to investigate its inhibiting behavior on corrosion of mild steel in hydrochloric acid solution.

2. Experimental

2.1. Material preparation

AR grade hydrochloric (Merck) and deionised water were used for preparing test solutions of 1N HCl for all experiments. The inhibitor was synthesized in the laboratory according to the procedure described elsewhere [12]. It was characterized through its IR and ^{1}H NMR spectral data and its purity was confirmed by thin layer chromatography. The name and structural formula of inhibitor is given in Fig. 1 .

2.2. Weight loss measurements

The experiments were carried out in 1N HCl using cold rolled mild steel samples of size 5.0 cm × 2.0 cm × 0.025 cm having composition: C = 0.14%, Mn = 0.35%, Si = 0.17%, S = 0.025%, P = 0.03% and the remainder as Fe. The experiments were performed as described earlier [13].

2.3. Electrochemical studies

For potentiodynamic polarisation studies, mild steel strips of same composition coated with commercially available lacquer with an exposed area of 1.0 cm^2 were used and experiments were carried out at constant temperature of 30 ± 2 °C as per ASTM, G 1-72.[14]. Potentiodynamic polarization studies were carried out using Gamery Potentiostat. A platinum foil was used as an auxiliary electrode and a saturated calomel electrode was used as a reference. IR compensated potentiodynamic polarisation curves for corrosion of mild steel in 1N HCl were recorded at 0.2 mV s^{-1}.

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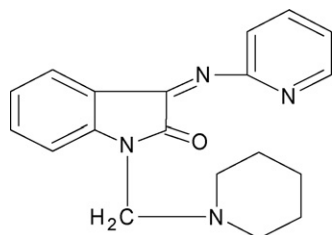E-mail address: maquraishi@rediffmail.com (M.A. Quraishi).

Fig. 1. Structure of N-(piperidinomethyl)-3-[(pyridylidene)amino]isatin (PPI).

3. Result and discussion

3.1. Weight loss studies

Table 1 shows the values of inhibition efficiency (IE) and corrosion rate (CR) obtained from weight loss measurements at different concentrations of Mannich base at 35 °C. From weight loss values, the %IE and surface coverage (θ) of each concentration were calculated using the following equations:

$$IE = \frac{CR_0 - CR}{CR_0} \times 100$$

$$\theta = \frac{CR_0 - CR}{CR_0}$$

where CR_0 and CR are the corrosion rates in the absence and presence of inhibitor, respectively.

It has been found that inhibition efficiency of the compound increases with increase in concentration (Fig. 2a). The maximum inhibition efficiency of 94% was found at 300 ppm concentration of inhibitor and further increase in concentration did not cause any significant change in the performance of inhibitor. The effectiveness of PPI is due to the lone pair and π-electrons present in the inhibitor molecule [15].

The variation of inhibition efficiency with immersion time is shown in Fig. 2b. It is found that inhibition efficiency increases from 94.1% to 100% with increase in immersion time from 3 to 24 h due to increased adsorption of inhibitor molecules on metal surface.

The variation of inhibition efficiency with temperature (Fig. 2c) reveals that increase in temperature from 35 °C to 55 °C does not show any significant change in inhibition efficiency, thereby, suggesting that the compound is effective corrosion inhibitor in acid solution up to 55 °C.

The variation of inhibition efficiency with increase in acid concentration from 0.5 to 3.0N is shown in Fig. 2d. It is found that inhibition efficiency decreases from 95.4% to 83.8% with increase in acid concentration due to increased aggressiveness of the acid solution.

The values of activation energy (E_a) were calculated using Arrhenius equation. A plot of log of corrosion rate obtained by weight loss

Table 1
Corrosion parameters for mild steel in aqueous solution of 1N HCl in absence and presence of different concentrations of inhibitor from weight loss measurements at 35 °C for 3 h of immersion time

Inhibitor concentration (ppm)	Weight loss (mg)	Inhibition efficiency (%)	Corrosion rate (mm year^{-1})
Blank	241.5	00.0	44.79
50	40.3	83.3	7.48
100	20.5	91.5	3.80
200	18.4	92.4	3.41
300	14.3	94.1	2.65

Table 2
Thermodynamic activation parameters for mild steel in 1N HCl in the absence and presence of the inhibitor (300 ppm concentration)

Thermodynamic parameters	1N HCl	PPI
E_a (kJ mol^{-1})	51.05	47.87
$-\Delta H$ (kJ mol^{-1})	40.84	36.18
$-\Delta S$ (J mol^{-1} K^{-1})	199.65	204.41
$-\Delta G_{ads}$ (kJ mol^{-1})	–	35.24
$-Q$ (kJ mol^{-1})	–	7.19

measurement versus $1/T$ gave a straight line (Fig. 2e). The value of activation energy (E_a) obtained from the slope of this line is given in Table 2. The free energy of adsorption (ΔG_{ads}) at different temperatures were calculated using the following equation [16]:

$$\Delta G_{ads} = -RT \ \ln(55.5K)$$

and K is given by

$$K = \frac{\theta}{C}(1 - \theta)$$

where θ is degree of coverage on metal surface, C is the concentration in mol l^{-1} and K is equilibrium constant. The value of ΔG_{ads} is given in Table 2.

The degree of surface coverage (θ) for optimum concentration of inhibitor in 1N HCl at 35–55 °C for 3 h immersion time has been evaluated from weight loss values. A plot of $\log(\theta/1 - \theta)$ versus $1/T$ gave a straight line (Fig. 2f). The value of heat of adsorption (Q) obtained from the slope of this plot is given in Table 2. Since the value of heat of adsorption is less than -40 kJ mol^{-1}, hence physical adsorption occurs [17].

The values of enthalpy of activation (ΔH°) and entropy of activation (ΔS°) were calculated using the following equation:

$$\text{rate} = \frac{RT}{Nh} \exp\left\{ \frac{\Delta S^\circ}{R} \right\} \exp\left\{ -\frac{\Delta H^\circ}{RT} \right\}$$

where h is the Planck's constant, N is the Avogadro's number and R is the general gas constant. A plot of $\log(CR/T)$ versus $1/T$ gave a straight line (Fig. 2g) with a slope of $(-\Delta H^\circ/2.303R)$ and an intercept of $[\{\log(R/Nh) + (\Delta S^\circ/2.303R)]$. The values of enthalpy of activation (ΔH°) and entropy of activation (ΔS°) obtained from slope and intercept of this line are listed in Table 2. It is found that the value of activation energy for inhibited system is lower than that for uninhibited system which indicates that the inhibitor exhibits high inhibition efficiency at elevated temperatures. The value of ΔH° is lower in presence of inhibitor indicating that the less energy barrier for the reaction in presence of inhibitor is attained and hence exhibit high inhibition efficiency at elevated temperatures [18]. The values of ΔS° in the absence and presence of inhibitor are large and negative. This indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering occurs on going from reactants to the activated complex [19].

The negative value of free energy of adsorption indicates spontaneous adsorption of inhibitor molecules on the surface of mild steel [18]. The value of ΔG_{ads} for inhibited system is less than 40 kJ mol^{-1} (9.56 kcal mol^{-1}) indicating that the inhibitor molecules on the surface of mild steel are physically adsorbed [20].

3.2. Adsorption isotherm studies

In order to understand the mechanism of corrosion inhibitor, the adsorption behaviour of organic adsorbate on the metal surface must be known [21]. The degree of surface coverage (θ) for different