Corrosion inhibition of mild steel using novel pyridine derivative in 1 M hydrochloric acid

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A novel pyridine derivative was synthesized, and its corrosion inhibition effects on mild steel in a 1M hydrochloric acid environment were investigated by gravimetric techniques. The results demonstrated that the inhibitive performance increased with the increasing of inhibitor concentration. At 303, the inhibition efficiency of pyridine derivative 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene accomplished 96.2% at the inhibitor concentration of 0.005 M. The mechanism of inhibition implicated the forming of a protective layer from inhibitor molecules on the surface of mild steel by a Langmuir adsorption isotherm. The presence of nitrogen and oxygen atoms in the structure of 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene confirmed by CHN-analysis revealed the adsorption of inhibitor molecules on the surface of mild steel surface.

INTRODUCTION

Generally, mild steel alloys are utilized in industrial processes and as a result it damages when exposed to different acidic solutions. The addition of corrosion inhibitors is the best technique to protect mild steel and other alloys from corrosive solution, such as hydrochloric acid solution [1-3]. The inhibition efficiencies of corrosion inhibitors are generally influenced by the inhibitor molecules' structures [4, 5]. A number of researchers were investigating deeply to the theme of corrosion inhibitors for mild steel in corrosive environment [6-8]. The most efficient inhibitors are organic molecules which having phosphorus, sulfur, oxygen, and nitrogen in the molecular structures in addition to double and triple bonds [9-11]. The inhibition mechanism of organic molecules is suggested as adsorption mechanism, which involves the unshared of electrons of the heteroatoms of inhibitor molecules react with the empty orbits of metal surface [12-14]. The organic compounds, such as pyridine [15] and Schiff base [16], have the ability to serve as adsorption sites in efficient inhibitor molecules due to the ability of these organic compounds give their unpaired of electrons

to d-orbitals of iron atoms [17]. In industries the addition of acids such as hydrochloric acid is the best technique for cleaning and other industrial processes. Generally hydrochloric acid is the main utilized acid in industries, due to economic reasons [18-20]. Hydrochloric acid causes corrode which were costly and replacement of the petroleum industry corroded equipment should be every year. To control or reduce the corrosion of mild steel during the process of acidizing, inhibitors should be adding [21-27]. In this study, a novel pyridine derivative has been synthesized and examined its inhibiting characteristics 1 M hydrochloric acid solution for mild steel on the basis of gravimetrical techniques. The effects of immersion time and temperature, were also studied.

EXPERIMENTAL

Preparation of coupons

The coupons for gravimetrical measurements were fabricated from mild steel strips with a composition wt % of C, 0.21; Mn, 0.05; Si, 0.38; P, 0.09; S, 0.05; Al, 0.01; and Fe, balance. The size of coupons was 5×1×0.3 cm. Previously to the measurements, the coupon was abraded with an emery papers and washed with distilled water, then with acetone. Finally, the coupons were dried and stored in an oven before use.

Preparation of solutions

All the experiments were conducted in 1 M hydrochloric acid in the absence and in presence of 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene as a corrosion inhibitor. The corrosive solution was prepared by adding distilled water to 37% hydrochloric acid of analytical grade. The concentrations of 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene were 1 mM, 2.0 mM, 3.0 mM, 4.0 mM and 5.0 mM.

Gravimetric techniques (weight loss measurements)

Mild steel coupons were immersed in 1M hydrochloric acid environments without and with various concentrations of 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene for period of time 1, 5, 10 and 24 h at different solution temperature 303, 313, 323 and 333 K. Then the coupons were removed and washed with water then acetone, dried, and weighed accurately. The experiments were conducted Triplicates for each experiment, and the mean was calculated. The corrosion rate (C_R) in ($\text{g m}^{-2} \text{h}^{-1}$) was determined using the Equation (1):

$$C_R = \frac{W_1 - W_2}{S \times t} \quad (1)$$

where W_1 (g) is the weight of a tested coupon in gram without inhibitor, W_2 (g) is the weight of a tested coupon in gram with the addition of inhibitor, S is the area of a tested coupon in m^2 , and t is exposure time in hour.

RESULTS AND DISCUSSION

Weight loss techniques

The inhibition performance of an organic compound for resisting metals corrosion depends on various parameters, such as the structure of the tested inhibitor, inhibitor concentration and the nature of the tested metal in addition to the temperature of the acidic solution. In the current investigation, mild steel coupons were utilized. The surface coverage (θ) and the inhibition efficiency (IE) were determined according to equations 2 and 3.

$$\theta = \frac{C_{Ro} - C_{R(\text{corr})}}{C_{Ro}} \quad (2)$$

$$IE = \frac{C_{Ro} - C_{R(\text{corr})}}{C_{Ro}} \quad (3)$$

where C_{Ro} is the corrosion rate in absence of corrosion inhibitor and $C_{R(\text{corr})}$ is the corrosion rate in the presence of corrosion inhibitor. The Standard Error of each point was calculated from dividing the Standard Deviation over the square of each point value.

The corrosion rate $C_{R(\text{corr})}$ the surface coverage and inhibition efficiency were determined from gravimetric techniques of mild steel coupons in 1M hydrochloric acid solution with different inhibitor concentrations and various immersion times are demonstrated in Figure 1. It is obvious that the studied inhibitor 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene was efficient in impeding the mild steel corrosion. At a relative exposure time of 10 hours, the inhibition efficiency increased with the concentration of the synthesized inhibitor. The highest inhibitive efficiency (IE) was 96.2%, which accomplished at a concentration of 0.05 M utilizing 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene. Considering the con-

centration of the acidic solution and exposure times, this value of inhibition efficiency is actually significant. The effects of the nitrogen atoms and resonance in 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene molecules on corrosion behavior can be concluded. As demonstrated in Figure 1, when the exposure time was increase, the inhibition efficiency increased whereas the rate of corrosion decreased. 4-Hydroxy-3-(pyridin-2-ylaminomethyl)toluene molecule acts as an inhibitor at early exposure times, but its efficiency decreases with time so that it accelerates corrosion after 24 h. The inhibition efficiency gradually decreased with the exposure period for 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene molecules which may be due to partial desorption of inhibitor molecule from the metal surface. The decrease in inhibition efficiency after a long period of immersion can also be attributed to a less concentration or limited number of available inhibitor molecules in HCl solution to stop or reduce metal dissolution; it is evident that after inhibitor molecules had been desorbed from the metal surface they become inactive and therefore did not take part in the inhibition process.

Fig. 1. Various corrosion rates and inhibition efficiencies with various inhibitor concentrations for periods of time for mild steel in 1 M HCl at 303 K (Continue on next page)

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Effect of temperature

The effect of Temperature on the Inhibitive performance is demonstrated in Figure 2, which show the inhibition efficiency of the studied corrosion inhibitor for mild steel in 1 M hydrochloric acid environment.

When the inhibitor concentration increased from 0.001 to 0.005 M, and the temperature increased from 303 to 333 K, the inhibition efficiency decreased with increasing temperature. This imputed to the desorption of 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene molecules from the mild steel surface at a rising temperature.

Fig. 2. Various corrosion rates and inhibition efficiencies with various inhibitor concentrations for different temperatures for mild steel in 1 M HCl at 5 h (Continue on next page)

Fig. 2. Various corrosion rates and inhibition efficiencies with various inhibitor concentrations for different temperatures for mild steel in 1 M HCl at 5 h

As yet, the opposite trend, that is, increased inhibitive performance with rising temperature, has been found just in a highly dilute acid environment with slightly raised temperature.

Adsorption isotherms

The adsorption type has been investigated in order to realize the inhibition mechanism. The adsorption of 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene molecules on the mild steel surface is a final stage in the corrosion impedance process [28,29]. Different isotherms, namely Frumkin adsorption isotherm, Langmuir adsorption isotherm and Temkin adsorption isotherm have been investigated in order to fit the methodological results. The correlation coefficient (R_2) has been utilized to select a proper adsorption isotherm. It was found from surface coverage parameter which accomplished from gravimetric techniques that the adsorption process of the 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene on the metal surface was best fitted with Langmuir isotherm (Equation 4).

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (4)$$

where θ is the surface coverage, C is the concentration of study inhibitor and K_{ads} is the adsorption constant.

$$\ln K_{\text{ads}} = \ln \frac{1}{55.5} - \frac{\Delta G_{\text{ads}}^0}{RT} \quad (5)$$

where 55.5 is the water concentration value

As in Equation (5) the adsorption process free energy (ΔG_{ads}^0) is associated with the K_{ads} .

Figure 3, demonstrates the relation between C/θ and concentration of 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene in hydrochloric acid solution with mild steel. From Figure 3, a significant correlation between C/θ and C was demonstrated for 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene with R_2 value of 0.98, that supposed that the process of adsorption follow Langmuir isotherm. The value of the slope of 1.19, for testing inhibitor, conclude that 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene molecules occupied more than one adsorption site on the mild steel surface. The ΔG_{ads}^0 is $-34.91 \text{ kJ mol}^{-1}$ which indicate that the adsorption process of the 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene on the mild steel surface is in the range of $20\text{--}40 \text{ kJ mol}^{-1}$, which indicate that the interaction of 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene molecules with the mild steel surface in 1 M hydrochloric acid solution is a physical-chemical sorption.

Fig. 3. Langmuir adsorption isotherm on the mild steel surface in presence of 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene at 303 K

Mechanism of inhibition

In general, the inhibition mechanism is nearly associated with the interaction between the inhibitor molecules and the metallic surface. Organic inhibitor, which has a heteroatom such as phosphorous, sulfur, oxygen and nitrogen, is the center of the reaction to

the adsorption process. Moreover, the steric hindrance and the polarity of the inhibitor molecule could affect the adsorption so the inhibitor efficiency would be affected. The 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene molecules as investigated inhibitor have one oxygen and two nitrogen atoms, so, this molecule has three adsorption sites, thus giving three coordination bonds with surface of mild steel. From experimental findings, the types of adsorption of the tested inhibitor at the mild steel-corrosive environment interface includes coordination bonds, and π -electrons of the pyridine ring with the metal surface. Figure 4, shows the suggested mechanism of inhibition.

Fig. 4. The suggested mechanism of 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene for mild steel in hydrochloric acid solution

CONCLUSIONS

The novel 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene was synthesized through a reduction reaction of Schiff base. The inhibitive efficiency for the mild steel in 1 M hydrochloric acid environment was studied through gravimetric techniques. The inhibitive efficiency increase with increasing the concentration of the 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene. At the same concentration, the inhibitor efficiency, reduce with increasing Temperature solution or the immersion time. At 303 K, the inhibition efficiency of the 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene reached to 96.2 % at the concentration of 0.005 M and immersion time 10 hours. The new compound 4-hydroxy-3-(pyridin-2-ylaminomethyl) toluene has significant properties as corrosion inhibitor in acidic solutions in high and low concentrations and working under high temperature and long exposure time conditions. The new inhibitor follow Langmuir adsorption isotherm and the interaction of 4-hydroxy-3-(pyridin-2-ylaminomethyl)toluene molecules with the mild steel surface Molecules in 1 M hydrochloric acid solution is a physical-chemical sorption.

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