Inhibition efficiency and corrosion rate studies of mild steel in nitric acid using 2-thioacetic acid – 5-pyridyl-1,3,4-oxadiazole complexes

Dina A. Najeeb

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq
E-mail: dinachem70@gmail.com

Abstract

The Schiff base 2-thioacetic acid – 5-pyridyl-1,3,4-oxadiazole and its complexes with metal ions Ni(II), Cu(II) and Co(II) have been examined as corrosion inhibitors of mild steel in 1 N HNO_3 solution by using weight loss technique. Data that we obtain shows good performance that these compounds are good inhibitors. The inhibition efficiency for the prepared ligand and its metal complexes increases with increasing their concentrations. The surface coverage values increase with increasing inhibitors concentration. The corrosion rate decreases as the concentrations of the ligand and its metal complexes increase. The inhibition efficiency of the ligand is less than that of its metal complexes and the inhibition efficiency of the metals follows the order Co>Ni>Cu. In the industries the inhibitors used widely due to anti-corrosive properties, but secondary effects may be shown which damage the environment. So the researchers began to prepare environmentally friendly inhibitors, like the prepared ligand and its metal complexes. At this time, some inhibitors are not being used in industrial processes due to their toxicity of chromate, phosphate and arsenic compounds, referring to different environmental and health troubles, so the governments must impose strict international laws. Inhibition behavior of the prepared ligand and its metal complexes has been attributed to their adsorption on the steel surfaces. The adsorption of the inhibitors obeys Langmuir adsorption isotherm for all tested systems. The surface morphology of mild steel was checked using a scanning electron microscope.

Keywords: *corrosion, inhibition, mild steel, nitric acid, adsorption.*

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Introduction

The problems of corrosion have gain considerable exploration because of the attack on materials. The nearly practical methods to resistance corrosion are use of inhibitors. The ability for corrosion it was reducing by adding small amounts (corrosion inhibitor) to a corrosive medium. Mild steel is an alloy of iron with carbon (carbon content 0.16–0.25%) which suffers corrosion easily in acidic medium. Mild steel alloys extremely utilized in engineering material in movement operators, the conversion of chemical industries, refining and petroleum manufacture, marine approach, fossil fuel power plant and nuclear power, structure and metal processing equipments [1]. The corrosion inhibitors have a considerable practical importance for utilizing in decrease metallic waste in engineering material [2]. Some metals having the capability to form-covalent bond with metals due to their free electron pairs like N, O and S [3]. The compounds that have π-bonds show good inhibitive properties due to effect of π-orbital that interact with the surface of metal [4]. The azomethine linkage that found in the prepared ligand have effective as potential corrosion inhibitors [5, 6]. Many complexes have been consider as corrosion inhibitors [7, 8]. The inhibitor that is added to acid solution to stop the damage correspond with the metal corrosion [9]. The metal complexes and its ligand are utilized to inhibit mild steel corrosion in acid mixture [10–14]. The heterocyclic rings that have N, S, P, O *etc*. in their structures act as the best corrosion inhibitors of metals with considerable activity mainly in aggressive acidic medium [15–17]. This study aims to investigate the inhibitory action of a Schiff base, 2-thioacetic acid – 5-pyridyl-1,3,4-oxadiazole (HL) and its metal ions complexes on mild steel corrosion in 1 N HNO_3 acid solutions.

2. Experimental details

2.1. Material preparation

Mild steel used in the research had the following weight percentage composition: C (0.15), P (0.36), Mn (0.6) and Si (0.03). Each coupon was washed in ethanol, dried in acetone and kept in a desiccator.

2.2. Electrolyte Preparation

One molar nitric acid solution was prepared by diluting appropriate volume of HNO_3 using distilled water. The concentration range of ligand and its metal complexes used was 100, 200, 300, 400 and 500 ppm and the electrolyte used was 50 ml for each experiment. The 2-thioacetic acid – 5-pyridyl-1,3,4-oxadiazole (HL) and its metal complexes were being prepared according to the procedure described previously [18]. Scheme (1) shows the preparation steps for the ligand.

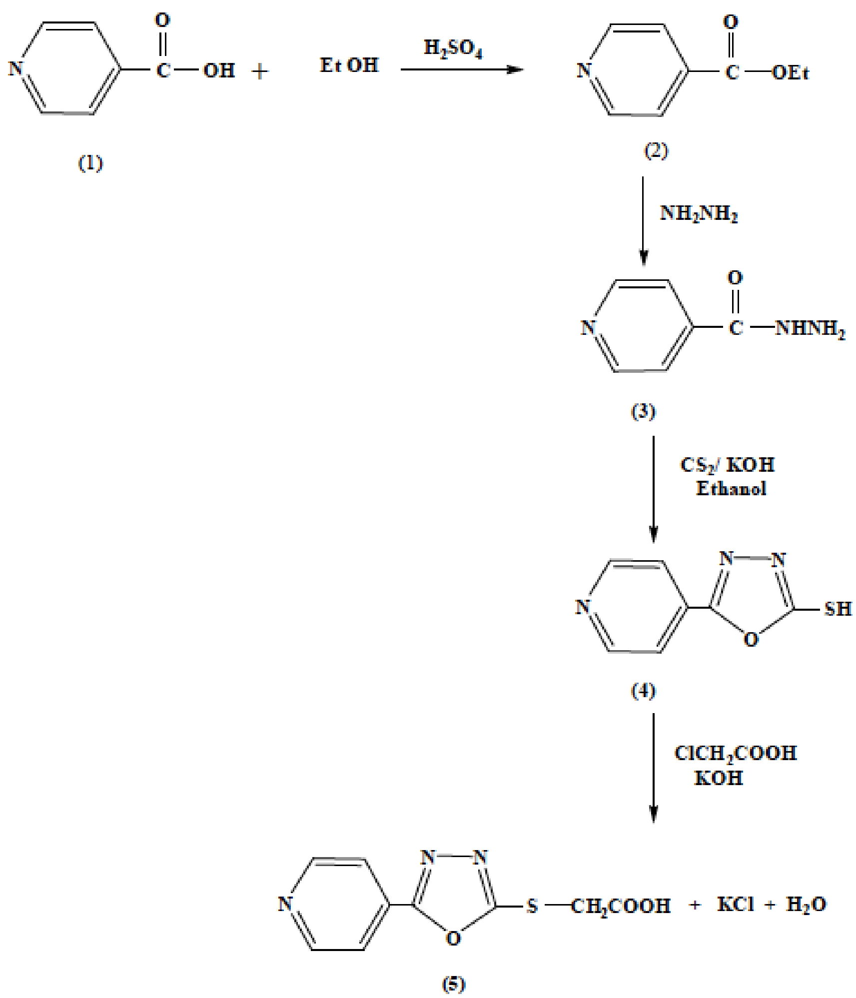
2.3. Weight loss measurement

For weight loss measurements, circular coupons were exposed to the acidic medium 1 N HNO_3. 50 mL of corrosive solution were put in a 100 ml glass beaker. The coupons were immediately immersed in the test solution without and with 100, 200, 300, 400 and 500 ppm of the ligand and its metal ions complexes. After 48 hours, the coupons were taken out, washed, dried, and re-weighed. The average weight loss mild steel coupons were obtained. The IE% and the (θ) of ligand and its metal ions complexes for mild steel corrosion were calculated using the following formula [19]:

$$IE\% = [W_U - W_i / W_U] \times 100 \qquad (1)$$

$$\theta = (W_U - W_i)/W_U \tag{2}$$

Where,
IE% = inhibition efficiency
θ = surface coverage
W_i = weight loss of mild steel in inhibited solution
W_U = weight loss of mild steel in blank solution



HL

Scheme 1. Reaction scheme for preparing ligand.

The corrosion rate (CR) has been estimated from this equation [20]:

$$CR = (-m_2)/S \cdot t \tag{3}$$

(m_1) and (m_2) are masses of mild steel alloy before and after corrosion respectively, S is the surface area of the coupons, t is immersion time.

2.4. Scanning Electron Microscope (SEM)

Surface analysis of the mild steel was investigated by using SEM apparatus type JEOL SEM 5800 with a probe having accelerator voltage of 20 keV. After 48 hours of immersion in the corrosive nitric acid solution (1 N) without and with various concentrations (100, 200, 300, 400 and 500) ppm of ligand and its metal ions complexes.

3. Results and Discussion

3.1. Weight loss studies

The weight loss data, inhibition efficiency, surface coverage and (corrosion rate) of mild steel in 1 N HNO_3 without and with 100, 200, 300, 400 and 500 ppm concentrations of (HL) and its metal complexes were respectively, tabulated in Tables 1 and 2. The data presented in Tables 1 and 2 show that the inhibition efficiencies increase with increasing inhibitors concentration. Similarly, surface coverage values increases with increasing inhibitors concentration due to the effect of adsorption of inhibitor molecules on the mild steel surface. The corrosion rate values decrease with increasing the concentrations of the prepared ligand and its metal complexes. Tables 1 and 2 data show that the ligand and its metal complexes behaves as a good corrosion inhibitors for mild steel alloy in 1 N HNO_3 solution at all concentrations. The prepared Schiff base has inhibition efficiencies towards mild steel alloy and this behavior may be assign to coordination by the (donor-acceptor) reaction between the unshared electron pairs of donor atoms of the ligand and its complexes [21]. Maximum inhabitation efficiency (89.719%) is obtained for 48 hours immersion of mild steel in 1 N HNO_3 solution containing 500 ppm of Co(II) complex.

Table 1. Weight loss, inhibition efficiency, surface coverage and corrosion rate data of mild steel corrosion at 48 hrs. Immersion in 1 N HNO_3 with different concentrations of prepared ligand.

Concentration ppm	Weight Loss (mg)	Inhibition efficiency	Surface Coverage	Corrosion rate (mg/cm^2·h)
Blank	321	–	–	1.362
100	132	58.878	0.5887	0.560
200	119	62.928	0.6292	0.504
300	102	68.224	0.8622	0.432
400	96	70.093	0.700	0.407
500	81	74.766	0.747	0.343

Table 2. Weight loss, inhibition efficiency, surface coverage and corrosion rate data of mild steel corrosion at 48 hrs. Immersion in 1 N HNO_3 containing different concentrations of Co(II), Ni(II) and Cu(II) complexes.

Concentration ppm	Weight Loss (mg)	Inhibition efficiency	Surface Coverage	Corrosion rate (mg/cm^2·h)
Co(II) complex				
Blank	321	–	–	1.362
100	75	76.635	0.766	0.318
200	69	78.500	0.785	0.292
300	54	83.177	0.831	0.229
400	47	85.358	0.853	0.199
500	33	89.719	0.897	0.140
Ni(II) complex				
100	95	70.400	0.704	0.403
200	86	73.208	0.732	0.364
300	75	76.635	0.766	0.318
400	63	80.373	0.803	0.267
500	52	83.800	0.830	0.220
Cu(II) complex				
100	102	68.224	0.682	0.432
200	92	71.339	0.713	0.390
300	84	73.831	0.738	0.356
400	70	78.193	0.781	0.297
500	62	80.685	0.806	0.263

The variation of inhibition efficiencies of mild steel corrosion in 1 N HNO_3 solution in the presence of ligand and its transition metal complexes at different concentrations is shown in Figure 1.

Figure 1 shows that the inhibition efficiency of the metal complexes is greater than that of the free ligand due to their huge size and molecular planarity [22]. Thus, the order of efficiency is as (CoL) > (NiL) > (CuL) > L.

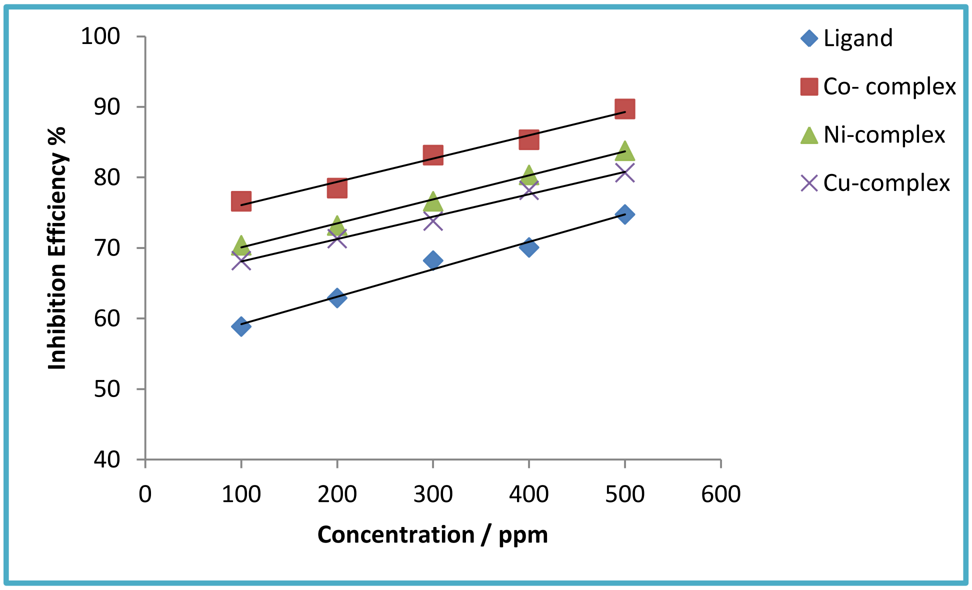


Figure 1. IE% against concentration of the prepared ligand and its metal complexes for mild steel corrosion in 1 N HNO_3 solution.

3.2. Adsorption isotherm

Langmuir isotherm found that all the adsorption sites are equal in value, and that atom bounding take place independently from nearby sites being cover or not. Under these conditions, surface coverage (θ) proportion to bulk concentration (*C*) of the adsorbing compound is as follows [23].

$$K_{\text{ads}}C = \theta/(1-\theta)$$

The K_{ads} is the adsorption (equilibrium constant) and *C* is the concentration of the inhibitors. K_{ads} values were obtained from the intercepts of the linear regressions between C/θ *versus* *C* for various inhibitors concentrations in the range from 100 to 500 ppm are shown in Figure 2 and the adsorption data are listed in Table 3.

The correlation coefficients data presented in Table 3 are very close to one which confirms that the adsorption of the inhibitor molecules in 1 N HNO_3 solution follows Langmuir adsorption isotherm.

K_{ads} data was concerning to the standard free energy of adsorption, ΔG^0_{ads} according to the following equation [23]:

$$K_{\text{ads}} = (1/55.5)\exp[(-\Delta G^0_{\text{ads}})/RT]$$

The term *R* referred to gas constant, *T* is the absolute temperature in Kelvin and 55.5 is constant which clarify the concentration of water in solution in mol/dm^3.

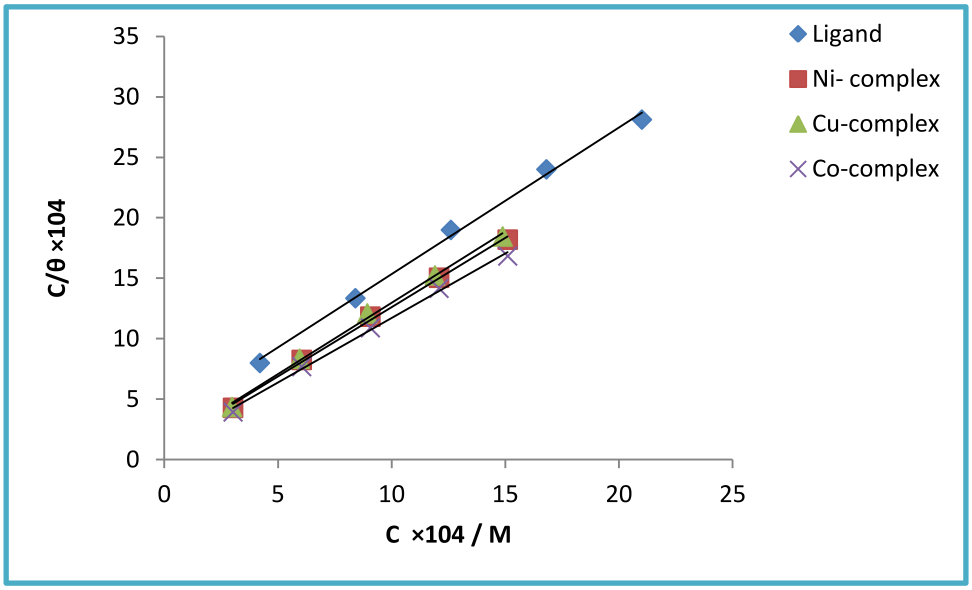


Figure 2. Langmuir isotherm plots for adsorption of the prepared ligand (HL) and its metal complexes on mild steel surface in 1 N HNO_3 solution.

Table 3. Thermodynamic quantities for adsorption of ligand and its metal ions complexes on mild steel.

Inhibitors	R^2	K_{ads} (10^4 M^{-1})	$-\Delta G$ (kJ mol^{-1})
Ligand	0.9994	4.241	30.650
Co-complex	0.9997	9.686	32.691
Cu-complex	0.9997	8.465	32.357
Ni-complex	0.9997	8.755	32.441

The average value of ΔG_{ads} is -32.03 kJ·mol^{-1}. The values of ΔG_{ads} which have negative sign refers to the spontaneity of the adsorption method and stability of the adsorbed layer on the external metal surface. Researchers propose that the range of ΔG_{ads} of chemical adsorption processes for the inhibitor lies between -21 to -42 kJ·mol^{-1} [23]. Therefore, in this present work the value of ΔG_{ads} has been suggesting within the range of chemical adsorption.

3.3. Scanning electron microscopy (SEM)

SEM (micrographs) gained from (unexposed) and (exposed) mild steel with 1 N HNO_3 solution for 48 h at 500 ppm Co(II) complex are shown in Figure 3. It can be detect that range of harm to mild steel surface is much less, the corrosion rate could be reduced when the inhibitors is added due to protective film adsorbed on transition metal surface, which show as a barrier and was accountable for the inhibition of corrosion.

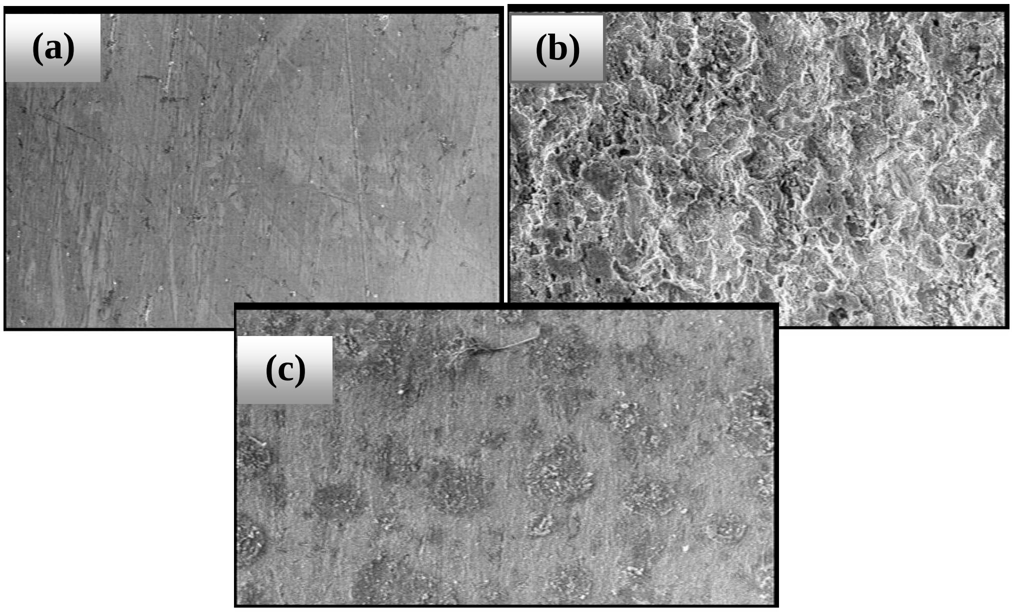


Figure 3. Scanning electron micrographs of mild steel alloy (a): unexposed polished alloy; (b): after immersion for 48 h. In 1 N of HNO_3 solution in absence of inhibitors (c): after immersion for 48 h. 1 N HNO_3 solution in the presence of 500 ppm of Co(II) complex.

Conclusion

The experimental weight loss results showed that the Schiff base ligand and its metal complexes are effective inhibitors for the corrosion of mild steel alloy in 1 N HNO_3 solution. The inhibition efficiencies values reveal that, these compounds inhibit the metal oxidation in acid medium. The maximum inhibition efficiency reached 89.719% for Co-complex which considered being the most effective inhibitor of mild steel corrosion in nitric acid solution. Langmuir adsorption isotherm gives a good explanation for the adsorption process for the ligand and its metal complexes on the mild steel surface. Gibbs free energy for adsorption data indicates that adsorption process is thermodynamically favorable and stable.

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