

1, 2(2, 2-dihydroxy Benzelidenamine) Phenyl Complexes as Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid

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Abstract

The corrosion inhibition on carbon steel in 1M HCl by 1, 2(2, 2-dihydroxy benzelidenamine) phenyl and its complexes was studied at different concentrations by "weight loss method". Data mark, for the compound shows good performance. These measurements show that the inhibition efficiency obtained by these complexes increased by increasing their concentration. The inhibition efficiency follow the order Co>Ni>Cu. The activation and adsorption thermodynamic parameters were determined and discussed. The surface coverage (Θ) of the inhibitors conform "Langmuir adsorption isotherm". (Morphology) of the carbon steel alloy has been examine using "scanning electron microscopy" in existence and inexistence of inhibitor.

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Keywords: Metal complexes, Schiff base, inhibition efficiency, Weight loss measurements.

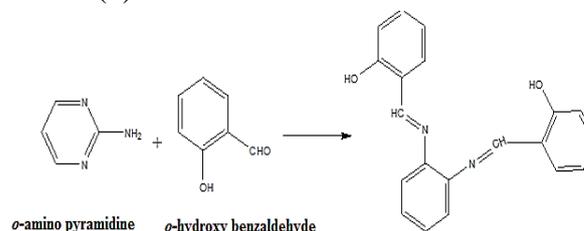
Introduction

A number of Schiff bases were known to be applicable as corrosion inhibitors for metal in acidic environments [1-4]. The main features of the prepared ligand with O, S and N as "polar groups" and conjugated double bonds in their shapes have been detected to be good "corrosion inhibitors" for so many complexes and alloys in corrosion media [5,10]. Carbon steel alloy has been used under so many different conditions in chemical and allied industries in handling alkaline, acid and salt solutions due to its good mechanical property. Adsorption of inhibitor is control by the electronic structure of the inhibiting complexes [11, 13], and also by steric factors, aromaticity, electron density at the donor atoms and also by the existence of functional groups such as C=NH, -N=N-, -CHO, R-OH, C=C, etc.. The Schiff base and its metal complexes effect on carbon steel corrosion in 1N HCl solution were studied by weight loss method for different concentrations. The realization of carbon steel alloy corrosion was always a major subject of great practical and theoretical benefit. Chloride, sulphate and nitrate ions in solution were especially "aggressive" so it speeds up corrosion. The best way to protect alloy from corrosion was to use corrosion inhibitors. 1, 2 (2, 2-dihydroxy benzelidenamine) phenyl and its complexes were prepared and characterized via (elemental analysis), FTIR, UV-Vis, (Molar conductance) and theoretical study in

previous work [14]. In this paper the inhibition efficiency of 1,2(2,2-dihydroxy benzelidenamine) phenyl and its complexes have been examined for the corrosion of carbon steel in 1M HCl.

2. Experimental details

Carbon steel alloy has purity more than 98.8% have been used in this research. The aggressive 1 M HCl was prepared by diluting the Analytical Grade 37% HCl with bidistilled water. The ligand and its metal complexes (Co, Ni and Cu) were being prepared according to the procedure described in paper [14]. The ligand prepared according to scheme (1).



Scheme (1): Reaction scheme for preparing ligand.

Inhibitor solutions with concentrations of 100 to 500 ppm being prepared by dissolving the required amount of the prepare Schiff base and its transition metal complexes in 50 ml of 1M HCl. The blank solution has been prepared as 50 ml of 1M HCl without inhibitor. Carbon steel specimens are cleaned with different grade emery papers and degreased with

acetone. The initial weight of each specimen was measured using an analytical balance and then the specimens were immersed in 1 M HCl solutions without and with different concentrations of the inhibitor for different time at room temperature. At the end, the specimens were washed and reweighed.

The (morphology surface)of corrosion output, on carbon steel sample after 24 h immersion in 1 M HCl in the existence and inexistence of 500 ppm of ligand and its metal complexes has been studied by SEM(inspect S50).

3. Results And Discussion

Weight loss measurements

The corrosion rate (CR) has been estimated from this equation [15]:

$$CR=(m_1-m_2)/S.t \dots\dots\dots(1)$$

(m_1) and (m_2) are masses of the specimen before and after corrosion respectively, S area of the specimen, t corrosion time.

The corrosion rate of the specimen immersed in 1 M HCl solution at various immersion time (1, 2 and 3) hours were 1.29, 1.86 and 2.80 mg/cm².h, respectively. After each immersion time the alloy be removed and cleaned. Dryish and reweight to obtain weight loss. Inhibition efficiency (PE %) was obtained by using the following equation [16] :

$$PE \%= (1 - CR / CR^\circ) \times 100 \dots\dots\dots(2)$$

CR and CR[°] are respectively, the corrosion rate (mg/cm²/h) of carbon steel specimen with and without inhibitor. Expression = (1-CR/CR[°]) was used to determine degree of surface coverage (Θ). When the concentration of inhibitor increase the inhibitor efficiency (PE %) increase. Amounts of (PE %), (CR) and (Θ) for Co complex at different concentrations and different periods of time are listed in Table(1).

Table (1)

PE%, CR and Θ by Co-complex calculated by mass loss test with carbon steel alloy in 1M HCl (Experiment periods: 1hour, 2 hours, and 3 hours).

Concentration ppm	Weight loss (mg)	PE %	Θ	CR (mg/cm ² .h)
100	1.2	60.5	0.605	0.510
200	0.8	62.1	0.621	0.489
300	0.4	63.33	0.633	0.473
400	0.2	66.6	0.666	0.431
500	0.09	68.2	0.682	0.411
Experiment period: 2 hours				
100	1.8	79.4	0.794	0.385
200	1.4	80.5	0.805	0.362
300	0.8	82.8	0.828	0.320
400	0.5	83.8	0.838	0.302
500	0.1	85.9	0.859	0.263
Experiment period: 3 hours				
100	2.2	87.7	0.877	0.345
200	1.7	88.8	0.888	0.315
300	1.3	89.7	0.897	0.289
400	1.1	90.0	0.900	0.279
500	0.7	92.5	0.925	0.211

Values of inhibition efficiency, corrosion rate and degree of surface coverage for Ni-complex at different concentrations and different periods of time are listed in Table (2).

Table (2)

%PE, CR and Θ by Ni-complexes evaluated by mass loss experiment with carbon steel in 1M hydrochloric acid (Experiment period: 1hour, 2 hours, and 3 hours).

Concentration ppm	Weight loss (mg)	PE %	Θ	CR (mg/cm ² .h)
100	1.6	53.8	0.538	0.596
200	1.3	59.3	0.593	0.525
300	0.6	59.8	0.598	0.519
400	0.5	65.4	0.654	0.447
500	0.4	65.7	0.657	0.443
Experiment period: 2 hours				
100	2	70.3	0.703	0.553
200	1.9	74.5	0.745	0.475
300	1.2	75.1	0.751	0.463
400	0.9	81.3	0.813	0.348
500	0.7	83.1	0.831	0.315
Experiment period: 3 hours				
100	2.8	86.0	0.860	0.392
200	2.3	86.8	0.868	0.370
300	1.8	86.9	0.869	0.366
400	1.6	88.8	0.888	0.315
500	0.9	89.0	0.890	0.309

The inhibition efficiency amounts, corrosion rate (CR) and degree of surface coverage (Θ) for Cu-complex with different

concentrations, and different time are listed in Table (3).

Table (3)

%PE, CR and Θ by Cu-complex calculated by mass loss test with carbon steel alloy in 1M HCl (Experiment period: 1hour, 2 hours, and 3 hours).

Concentration ppm	Weight loss (mg)	PE %	Θ	CR (mg/cm ² .h)
100	2.5	45.1	0.451	0.709
200	2.1	45.3	0.453	0.705
300	1.6	48.1	0.481	0.669
400	1.3	48.9	0.489	0.659
500	0.8	52.8	0.528	0.609
Experiment period: 2 hours				
100	3.1	63.3	0.633	0.682
200	2.8	63.8	0.638	0.673
300	2.4	66.4	0.664	0.625
400	1.7	71.1	0.711	0.539
500	1.2	73.7	0.737	0.490
Experiment period: 3 hours				
100	3.5	78.6	0.786	0.598
200	3	80.6	0.806	0.544
300	2.9	81.8	0.818	0.511
400	2.3	82.3	0.823	0.496
500	1.6	83.1	0.831	0.475

It is obvious from Tables 1, 2 and 3 that all these complexes inhibit the corrosion of carbon steel alloy at all concentrations have already been used in this work. The (PE %) for all of these complexes increases as concentrations of metal complexes increase. The information that we obtain from this study showed appreciable corrosion inhibition of the metal complexes disposal against corrosion of carbon steel alloy in a 1M HCl

solution. The Schiff base has inhibition efficiencies towards the carbon steel may be expected to coordination by the (donor-acceptor) reaction between the unshared electron pairs of donor atoms of the ligand and its metals [17, 18]. Weight loss measurements of carbon steel decrease with increasing concentrations of ligand and its metal complexes as shown in Figures 1, 2 and 3.

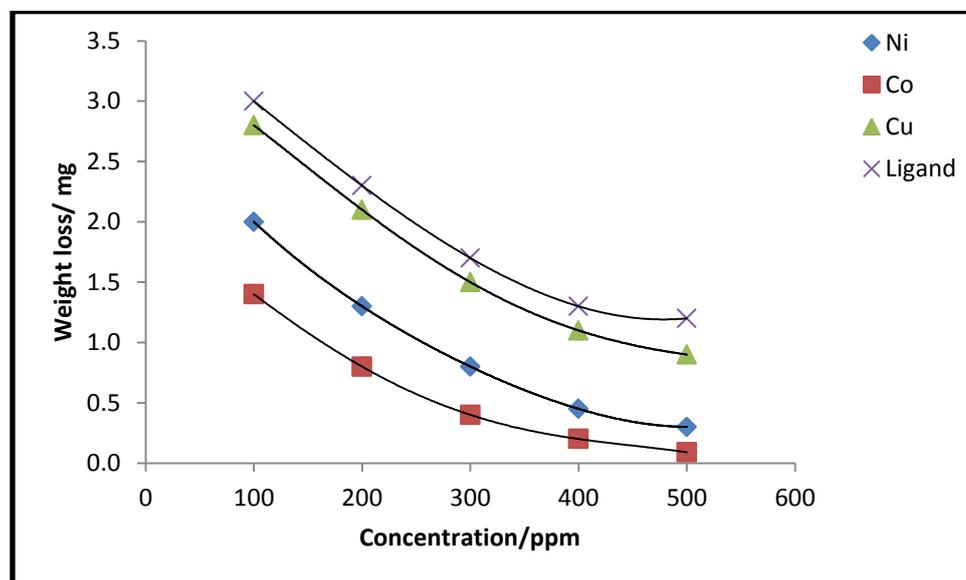


Fig.(1): Weight loss test for carbon steel versus concentrations in 1M HCl in the absence and occurring of Ni, Co and Cu complexes and its ligand for 1 hour.

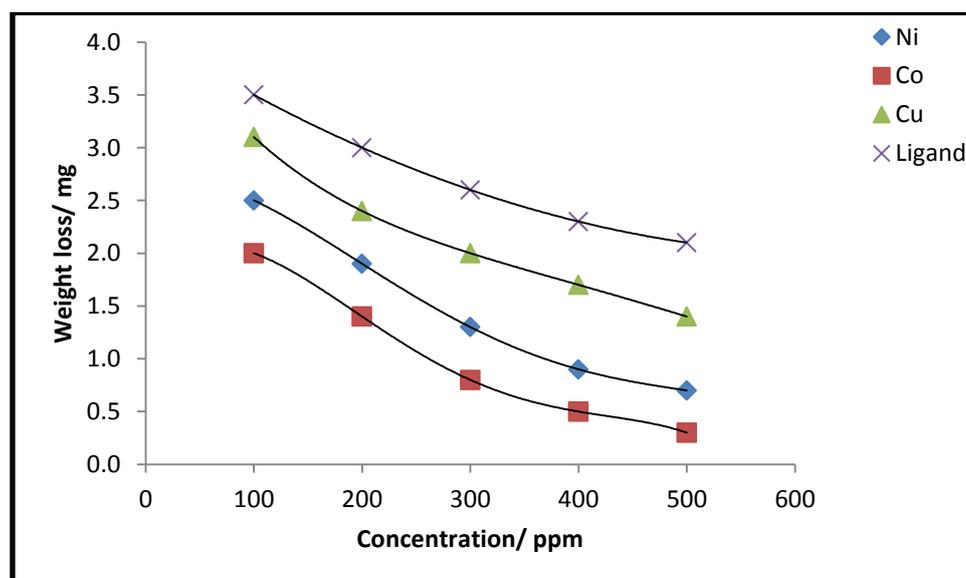


Fig. (2): Weight loss test for carbon steel versus concentrations in 1M HCl in the absence and occurring of Ni, Co and Cu complexes and its ligand for 2 hours.

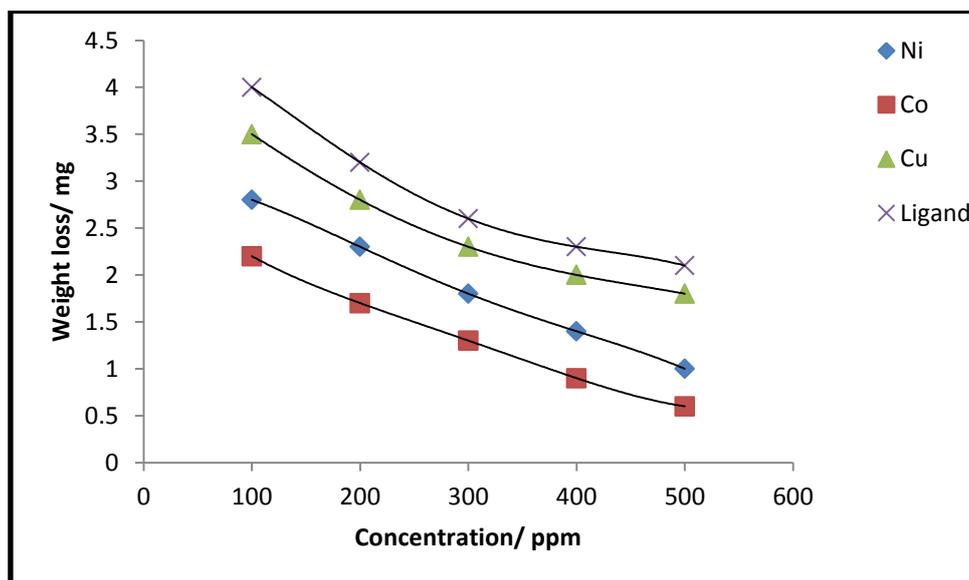


Fig. (3): Weight loss test for carbon steel versus concentrations in 1M HCl in the absence and presence of Ni, Co and Cu complexes and its ligand for 3 hours.

The inhibition efficiency increased with increased concentration of the metal complexes. This suggests that corrosion inhibition is a result of adsorption of inhibitor on the metal surface and the complexes acts as adsorption inhibitors. Best inhibition efficiency at excessive concentration may be indicating a larger coverage of metal with inhibitor molecules [19,21]. Difference in inhibition efficiency might be due to the difference in the stability and solubility of complexes in the acid solution. The metal complexes exhibit greater inhibition efficiency than the free ligand. The metal complexes

show great efficiency than Schiff base may be referring to their larger size and molecular planarity. Thus, the order of inhibition efficiency is Co-complexes > Ni-complexes > Cu-complexes > Ligand [22].

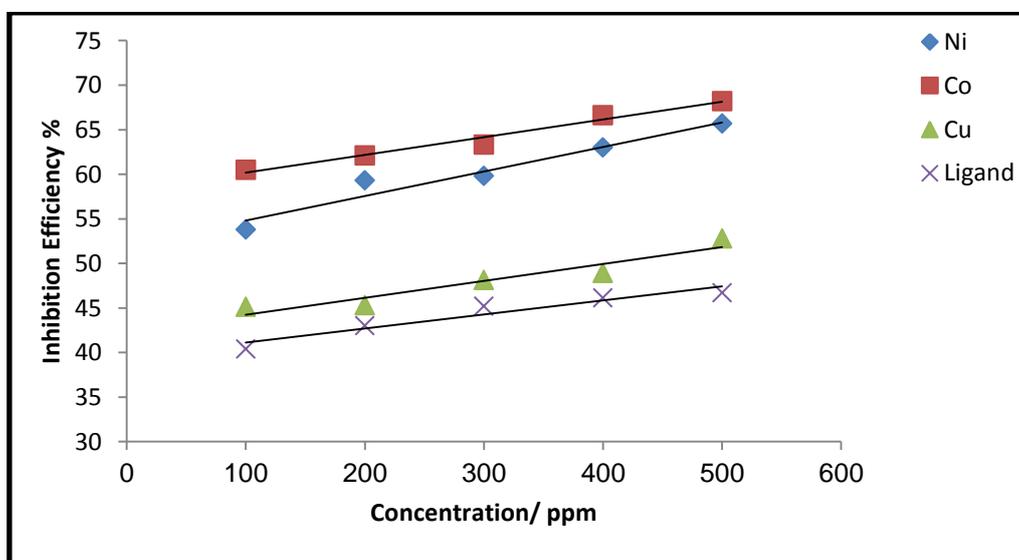


Fig.(4): The %PE against concentration of metal complexes and its ligand for carbon steel (immersion time: one hour).

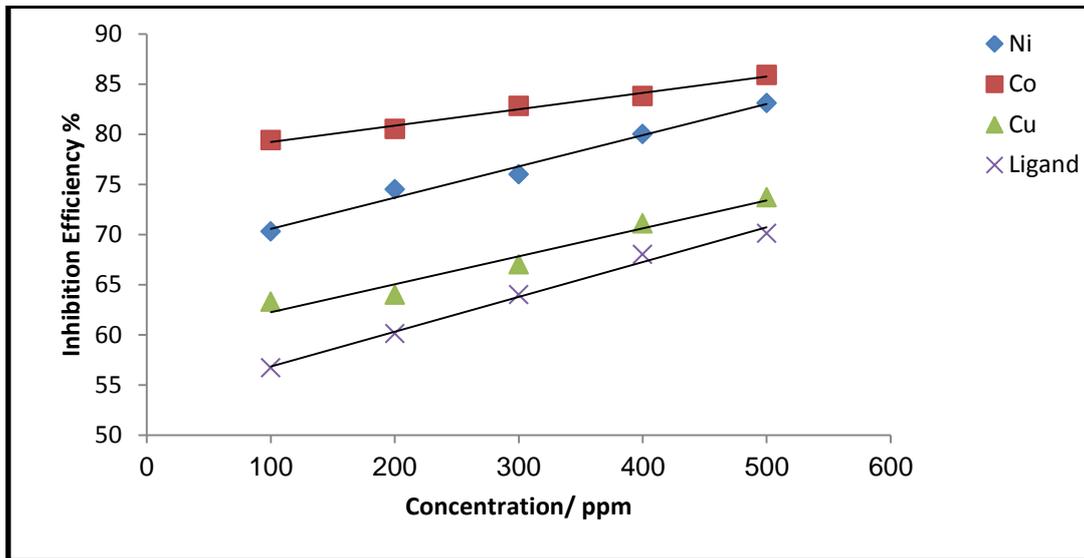


Fig.(5): The %PE against concentration of metal complexes and its ligand for carbon steel (immersion time: two hours).

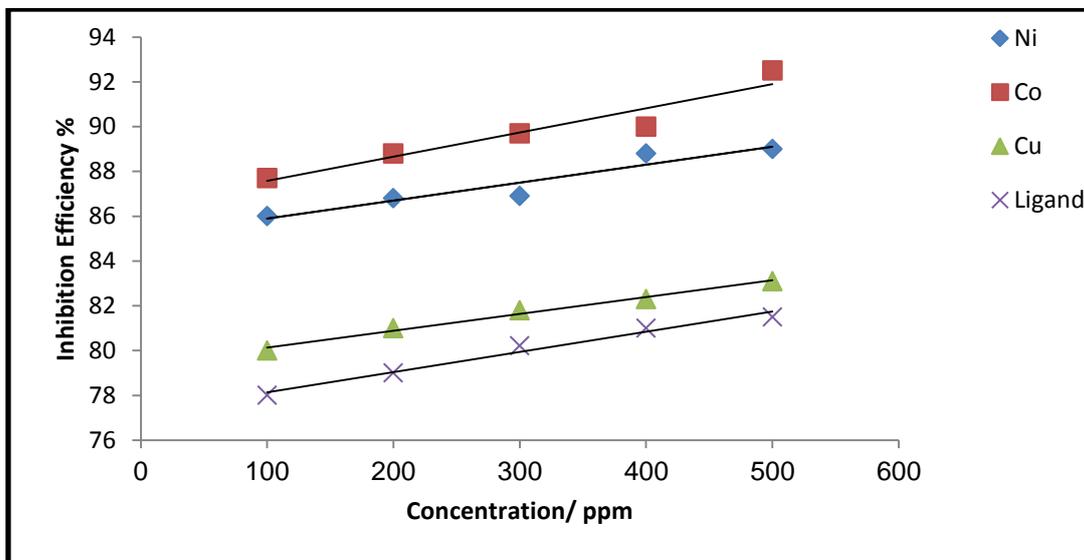


Fig.(6):. The %PE against concentration of metal complexes and its ligand for carbon steel (immersion time: three hours).

Corrosion kinetics of carbon steel in HCl acid with inhibitor

Figures 7, 8 and 9 show Log $W_i / \Delta W_t$ (initial weight over difference weight of carbon steel at time t) is variation with time for each complex. The straight lines, which complemented that the reaction with carbon steel alloy obeys first order reaction law [23, 24].

$$\text{Log } W_i / \Delta W_t = -k/2.303t - \text{log } W_i \dots \dots \dots (3)$$

The rate constants (k) measured from figures 7, 8 and 9 are listed in Table (4).

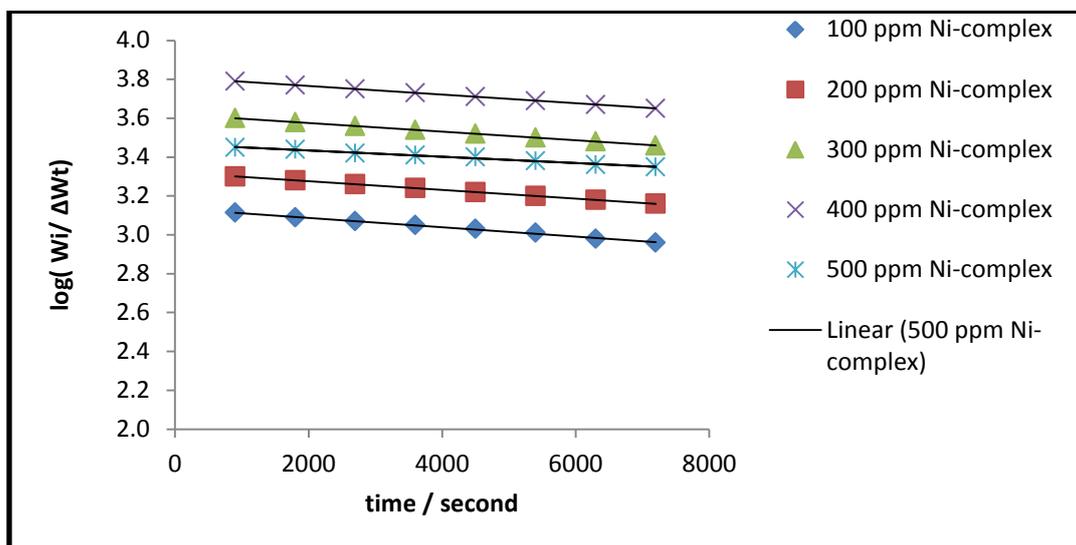


Fig.(7): Kinetic measurements of corrosion for carbon steel in HCl at different concentrations of Ni- complexes.

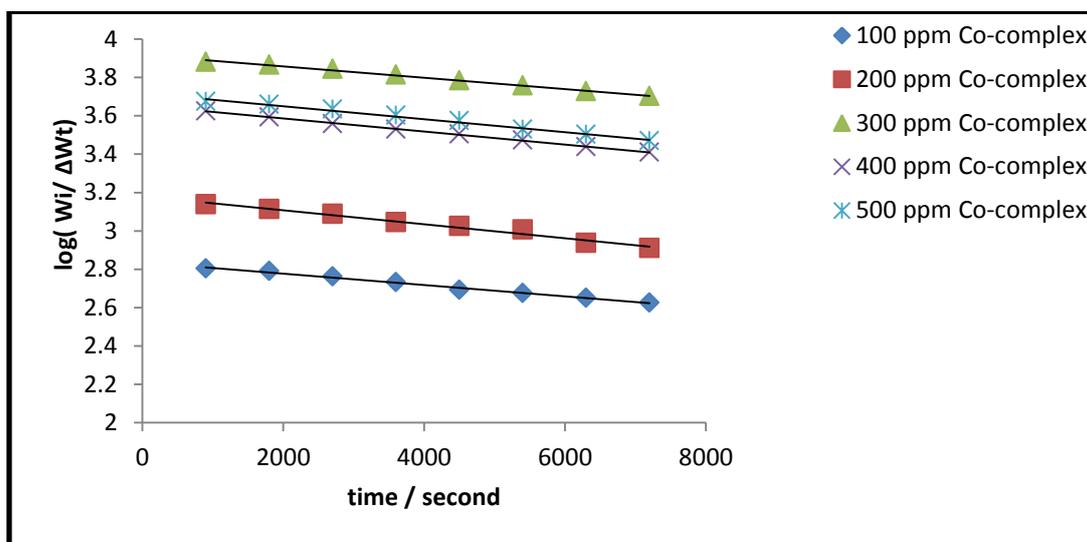


Fig.(8): Kinetic measurements of corrosion for carbon steel in HCl at different concentrations of Co- complexes.

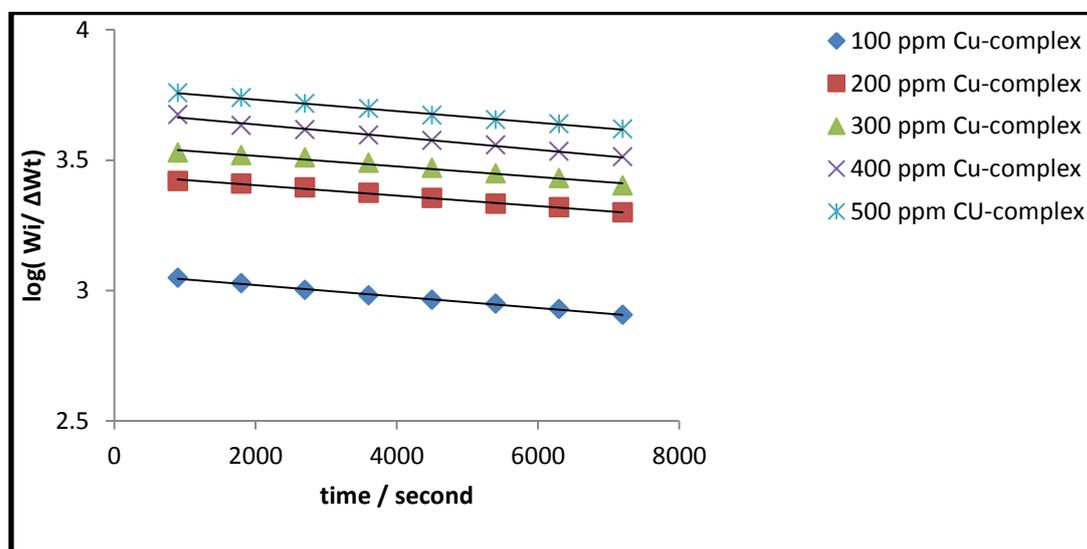


Fig.(9): Kinetic measurements of corrosion for carbon steel in HCl at different concentrations of Cu- complexes.

Table (4)
Kinetic measurements for carbon steel in 1M HCl with Ni-, Co- and Cu-complexes at different concentrations.

Conc. (ppm)	k(s ⁻¹)x10 ⁻⁵
Ni-complexes	
100	5.56861
200	5.11720
300	5.11720
400	5.11720
500	5.11720
Co-complexes	
100	7.82144
200	7.82144
300	7.82007
400	7.82007
500	7.82007
Cu-complexes	
100	5.08272
200	5.08272
300	5.08272
400	5.08272
500	5.08272

Thermodynamic study of carbonic steel in acid medium with inhibitor:

Fig.(10) shows that adsorption of organic metal complexes on carbon steel surface follow Langmuir isotherm [25]:

$$[C_{inh}/\Theta] = 1/k_{ad} + C_{inh} \dots\dots\dots (4)$$

Where k_{ad} is the equilibrium constant of adsorption constant, C_{inh} the concentration of inhibitor and Θ is the surface coverage. According to eq. (4). We can calculate k_{ad} . From the intercept lines from fig.10, so we can calculate the Standard free energy of adsorption (ΔG_{ads}^0) with following equation [26]:

$$\Delta G_{ads} = -RT \ln (55.5K_{ads}) \dots\dots\dots (5)$$

R is gas constant and T is absolute temperature. The value 55.5 is the concentration of water in solution in mol/dm³. It is found that the ΔG_{ads} values for the using ligand and its complexes are less than -40 kJ mol⁻¹, the negative values of ΔG_{ads} show spontaneous adsorption of metal complexes onto carbon steel [27]. Values of calculated free energies are listed in Table (5).

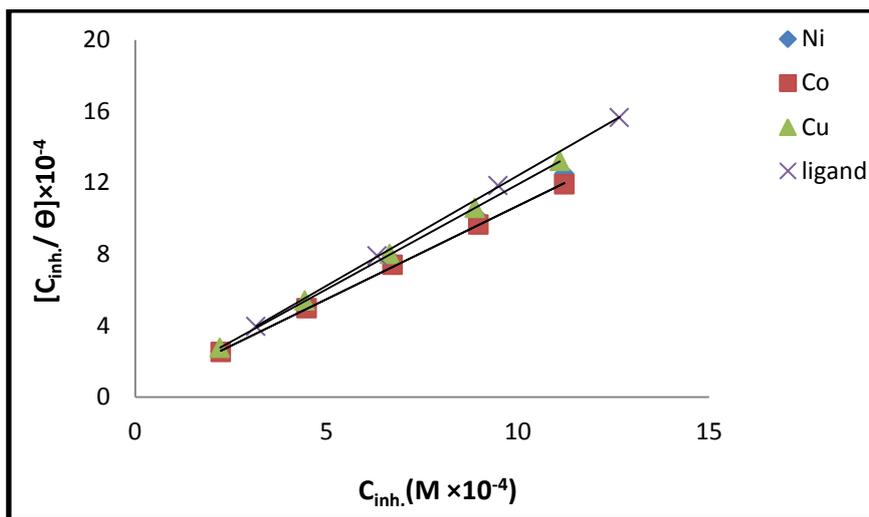


Fig.(10): Langmuir adsorption isotherm for carbon steel in 1M HCl without and with metal complexes.

Table (5)
Thermodynamic measurement of adsorption of metal complexes on carbon steel.

Inhibitors	R ²	K _{ads} (10 ⁴ M ⁻¹)	-ΔG / kJ mol ⁻¹
Ni-Ligand	0.9996	7.5019	37.763
Co-Ligand	0.9997	19.0114	40.066
Cu-Ligand	0.9996	4.0634	36.244
Ligand	0.9999	1.7864	34.208

Scanning electron microscopy (SEM)

SEM micrographs resulted from exposed and unexposed specimen in 1 M HCl for (24 hour) in the existence and inexistence of 500 ppm of the prepared ligand and its transition metal complexes are shown in Fig.(10). The scanning electron microscopy (SEM) has been used to study the morphology of the corroded surface in the existence and inexistence of inhibitor for the immersion of 24 hour at room temperature. The SEM images are taken from that portion of the specimen where good information is predictable. After corrosion tests, a surface analysis was carried out using scanning electron microscope, immediately. The rate corrosion (CR) was reduced extremely in the presence of inhibitors. It detect that there is a good preventative film adsorbed on metal surface, which acted as a barrier and was accountable for the inhibition of corrosion.

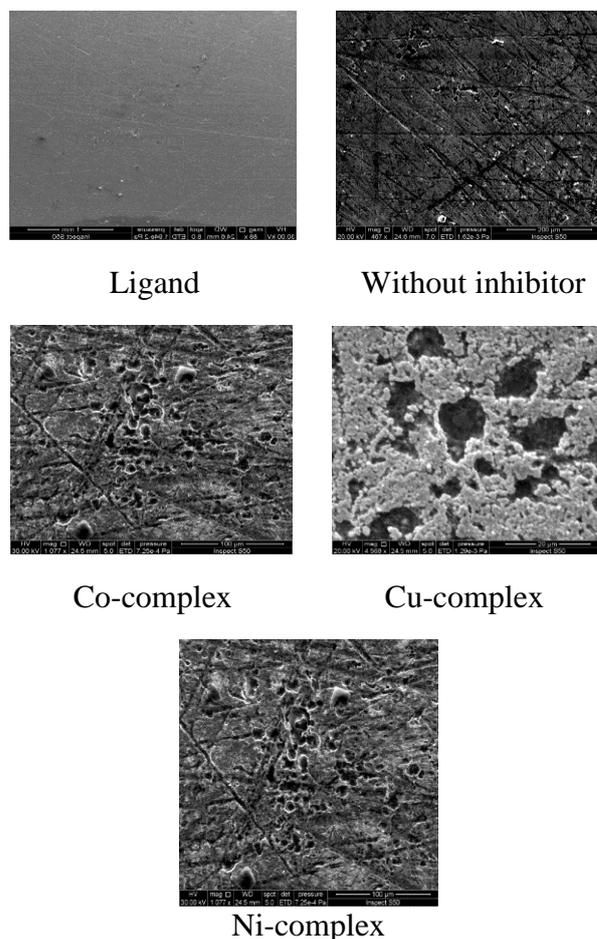


Fig.(11): Scanning electron micrographs of Ligand and its Complexes on carbon steel alloy.

Conclusions

These conclusions may be estimate from this research:

1. Data gained show that metal complexes show efficient inhibitors.
2. Inhibition efficiency increases with the increase of concentrations of metal complexes.
3. The value of ΔG°_{ads} is negative so it signs to spontaneous adsorption on the surface of metal.
4. 4-SEM checking of carbon steel surface showed the existence of protective surface film formed on carbon steel alloy surface which inhibits metal degradation in HCl.

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