



Inhibition of Zinc Corrosion in Hydrochloric Acid by Some Ligands and Complexes

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ABSTRACT

The corrosion inhibition of zinc in 2M HCl solution by thiourea, ligands, and complexes has been studied with respect to their concentrations. The corrosion rates were measured by using gasometric technique. The inhibition efficiency of each inhibitor increases and decreases with increasing its concentration in the range of, inhibition action and missing inhibition action respectively. Zinc surface coverage (θ) could be obtained from the corrosion rates in 2M HCl solution in absence and presence the used additives by gasometric technique. The inhibitors appear to function through adsorption following langmuir's isotherm. The free energy change of adsorption (ΔG_{ads}), enthalpy change (ΔH_{ads}), entropy change (ΔS), and activation energy (E_a) associated with each inhibitor have been determined. The heat of adsorption (ΔH_{ads}) and free energy of adsorption (ΔG_{ads}) of all inhibitors are negative values

KEYWORDS : gasometric technique; corrosion inhibition; zinc; Schiff base; hydrochloric acid

INTRODUCTION

Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous. Studies of the effect of organic additives on the corrosion rate of zinc have been the subject of many investigators⁽¹⁻⁵⁾. In acidic medium hydrogen evolution reaction predominates. Corrosion inhibitors reduce or prevent these reactions.

Generally the organic compounds containing hetero atoms like O, N, and S are found to have function as very effective corrosion inhibitors. The efficiency of these compounds depends upon the number of adsorption active centers in the molecule, their charge density, molecular size, and mode of adsorption⁽⁶⁻⁹⁾. Compounds contain electron-donating groups that decrease the corrosion rate by increasing the hydrogen over-voltage on the corroding metal⁽¹⁰⁾.

In the present work the corrosion of zinc was tested in 2M hydrochloric acid solution in absence and presence of inhibitors; such as thiourea, some ligands, and complexes, by gasometric technique. The aim of this study is to calculate the inhibition efficiency, and some thermodynamic parameters in the reaction of zinc metal in 2M HCl solution with and without the used inhibitors.

EXPERIMENTAL

Material and Sample Preparation:

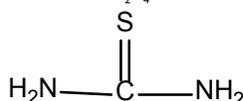
Zinc metal purity of 99.99% was used in gasometric technique. The samples of zinc associated with different surface area. A specific surface area of each sample was calculated. The surface of zinc sample was polished prior to any experiment with 600 grit SiC paper, rinsed with distilled water and polished with acetone –saturated paper towel to remove any grease⁽¹¹⁾.

The Electrolyte Media :

All chemicals, thiourea, ligands, complexes, and HCl were high purity. Bi-distilled water was used to prepare all solutions. The concentration of each used electrolyte was written in results and discussion. The experiments of gasometric technique were carried out at 30 °C in the most tested electrolytes and other experiments at different temperatures 35°C, 40°C, and 45 °C.

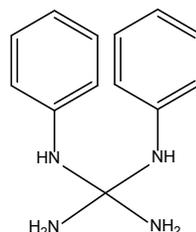
The Chemicals and their Structures:

Thiourea : CN_2H_4S (M.wt =76 gm)

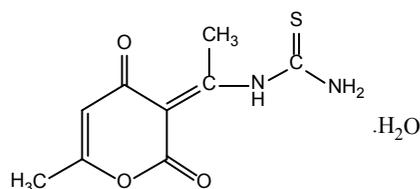


Ligands:

Ligand of (C₁₃H₁₆N₄) (M.wt =228 gm)

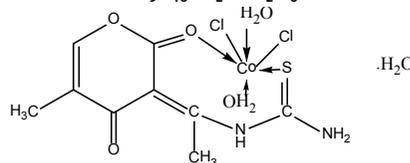


Ligand of (C₉H₁₂N₂O₄S) (M.wt =244 gm)

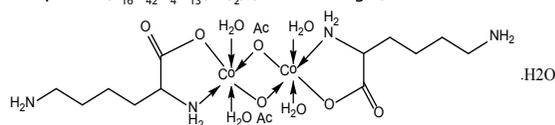


C- Complexes

Complex of (C₉H₁₆Cl₂CoN₂O₈S) (M.wt =409.8 gm)



Complex of (C₁₆H₄₂N₄O₁₃(Co)₂) (M.wt =616 gm)



Gas Evolution Measurements :

The reaction cell used for gas evolution reaction and the procedure of calculation of the rate of zinc dissolution in aggressive solutions were the same as described elsewhere^(12,13).

RESULTS AND DISCUSSION :

Figure (1) displays a relation between the volume of H₂ gas evolved (ml / cm²) versus time (minute), for the reaction between zinc of specific surface area and 50 ml HCl solution of different concentrations. It is essential to note that the curves of the reactions between zinc and hydrochloric acid increase after the elapses of a certain time from the immersion of zinc metal in the test solution. This time is identified as the incubation period which is the time needed by the acid destruct the pre-immersion oxide film and start dissolution of the zinc sample to give H₂ gas. After this incubation period, the volume of H₂ gas evolved increases linearly with time due to possible simultaneous destruction of zinc passive film and continuous dissolution of the metal sample. The slope of the linear regions of the curves of this figure is taken as a measured of the corrosion rate of zinc in different concentrations of hydrochloric acid solution⁽¹⁴⁾. It is essential to note also from the figure that the rate of reaction increases with increasing the acid concentrations.

Figures (2,3) offer the variation of the volume of H₂ gas evolved (ml / cm²) as a function of time for the reaction of Zinc in 2M HCl solution in absence and presence of different concentrations of ligand (C₁₂H₁₆N₄) and complex (C₉H₁₆Cl₂CoN₄O₆S). Similar figures are obtained for other inhibitors of different concentrations, thiourea (CN₂H₄S), ligand (C₉H₁₂N₂O₄S), and complex (C₁₆H₄₂N₄O₁₃(CO)₂) in 50 ml of 2M HCl, not shown. It is essential to note from figure 2 and the like that, the corrosion rate (ml H₂ /cm²dt) and the incubation time of the reaction of zinc in 2M HCl in presence inhibitors (CN₂H₄S, C₉H₁₂N₂O₄S) decrease and increases respectively than the corrosion rate of zinc in 2M HCl only with increasing the concentrations of additives from 10⁻⁶M to 10⁻⁵M. This case was simply related to the inhibiting action of the used additives in this concentration range.

On the other side, figure 2 and the like (not shown) reveal the corrosion rate and the incubation time of zinc reaction in the same aggressive media increases and decreases respectively than the corrosion rate of zinc in 2M HCl only with increasing the concentration of additives from 10⁻⁴ M to 10⁻² M. Some workers⁽¹⁵⁾ demonstrate the enhancement of corrosion rate to the reduction of major quantity of thiourea at high concentrations, and hence, produce a valanche quantity of corrosion promoting species, e.g. HS⁻ ion, to promote corrosion reaction. But in our work this phenomenon occurs also in presence of a complex without thiourea (C₁₆H₄₂N₄O₁₃(Co)₂). Therefore, this case may be due to the reduction potentials of these inhibitors increase with increasing their concentrations to more positive values than the reduction potential of zinc and hence accelerate the anodic dissolution of zinc.

It is essential to note from figure 3 and the like (not shown) that some curves tell us inhibiting action of the used additive complexes at low concentrations and others reveal missing of inhibiting efficiency at high concentrations. This also may be to destruction of major quantity of complexes by reduction and hence accelerate the oxidation reaction of zinc.

The values of A° and A, the corrosion rate of zinc in 2M HCl in absence and presence of the used additives in the concentrations range of the inhibition efficiency, were calculated from figures 2,3 and the like (not shown). This is due to evaluate the inhibition efficiency (I), and the zinc surface coverage (θ) for different additives of different concentrations according to the following relations respectively⁽¹⁶⁻¹⁷⁾.

$$I = \left(1 - \frac{A}{A^\circ}\right) \times 100 \dots\dots\dots (1)$$

$$\theta = \left(1 - \frac{A}{A^\circ}\right) \dots\dots\dots (2)$$

The values I, θ and the evaluated C_{inh}, θ of the used additives at different concentrations in the range of inhibition efficiency are listed in tables (1, 2).

Figures (4,5) represent the Langmuir's adsorption isotherm (C_{inh},M / θ versus C_{inh},M) of the used inhibitors, thiourea, ligands attached thiourea, and the used complexes in 2M HCl. It is essential to note from these figures that the experimental data obtained from gasometric technique could fit the Langmuir's adsorption isotherm. The value of K_{ads} of each additive in the reaction of zinc in 2M HCl was calculated according to the following relation^(16,19),

$$C_{inh} / \theta = \frac{1}{K_{ads}} + C_{inh} \dots\dots\dots (3)$$

Where K_{ads} is the equilibrium constant of the adsorption process, is the strength for the adsorption force between the inhibitor molecules and the metal surface, C_{inh} is the inhibitor concentration, and θ is the zinc surface coverage with each inhibitor at definite concentration.

The value of the free energy of adsorption of each inhibitor (ΔG_{ads} in KJ mol⁻¹) on the surface of zinc reacted with 2M HCl was calculated by using the following equation^(20,21) and listed in table 3.

$$K_{ads} = \frac{1}{55.5} + e^{-\Delta G_{ads} / RT} \dots\dots\dots (4)$$

Where 55.5 is the concentration of water in the solution in mol / L, R is the general gas constant in J mol⁻¹K⁻¹, and T is the absolute temperature.

Figure (6) and the like (not shown) display the variation of the volume of H₂ gas evolved (ml / cm²) as a function of time for the reaction of zinc in 2M HCl solution in presence 5x10⁻⁶ M ligands and 5x10⁻⁷ M of complexes at different temperatures.

It is essential to note from figure 6 and the like (not shown) that the corrosion rate of zinc in 2M HCl in presence definite concentration of additive increases with increasing the temperature of the reaction. In the other word, the inhibition efficiency of each used inhibitor decreases with increasing the temperature. This case was simply related to the desorption is aided by increasing the temperature. This confirms to us that the adsorption mechanism of the used inhibitors on zinc surface in 2M HCl solution is through physisorption type⁽²²⁾. However the chemisorption process^(23,24) accompanied by an increase of the inhibitor inhibition efficiency with increasing the temperature of the reaction.

The activation energy (E_a), enthalpy change(ΔH) and entropy change (ΔS), of the reaction of zinc with 2M HCl in presence 5x10⁻⁶M of the used ligand and 5x10⁻⁷M of the used complex, were calculated according to the following Arrhenius and transition state equations respectively^(21,25,26)

$$\log K (rate) = \log A - \frac{E_a}{2.303 RT} \dots\dots\dots (5)$$

$$\log \frac{K(rate)}{T} = \log \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \dots\dots\dots (6)$$

Where K is the corrosion rate, R is the general gas constant, T is the absolute temperature, A is the Arrhenius constant depends on metal type and electrolyte, N is the Avogadro's number, h is the plank's constant.

Figure (7) and the like (with the tested complexes not shown) represent log K versus 1/T, according to equation 5, for zinc dissolution in 2M HCl in presence 5x10⁻⁶ M and 5x10⁻⁷M of different ligands and complexes respectively. Straight lines were obtained with slope equals -E_a/2.303R. The value of E_a of each ligand and complex at the definite concentration was calculated and listed in table 3.

Figure (8) and the like (with presence ligands, not shown) represent log K/T versus 1/T, according to equation 6, for zinc reaction in 2M HCl in presence 5x10⁻⁷ M and 5x10⁻⁶ M of different complexes and ligand respectively. This relation gave straight line with slope equals ΔH/2.303R and the intercept is . The values of ΔH and ΔS of each used inhibitor adsorbed on the zinc surface

during the reaction process between zinc and 2M HCl were calculated and listed in table 3.

It is essential to note from table 3 that ΔH values of the all used ligands and complexes are negative. This case was simply related to the adsorption process of the used inhibitors on zinc surface is exothermic. Table (3) clears also that, ΔH values of the all tested inhibitors (thiourea, ligands, and complexes) vary from 26.844 26KJ/mol to 38.26KJ/mol, in physisorption range from 8-40 KJ/mol .This confirms to us that the adsorption process is due to physisorption type. However chemisorption process varies from 40-400 KJ/mol ⁽²⁴⁾.The value of ΔS are also negative, this implies a decrease in randomness of inhibitors molecules from non- adsorption to adsorption process on the surface of zinc in the reaction medium. The negative sign of the free energy of adsorption (ΔG_{ads}) indicates that the adsorption of the inhibitor at zinc surface is a spontaneous process ⁽²⁵⁾.

Table 3 reveals also that E_a values in the presence of the used complexes greater than that in the presence of thiourea or the used ligands. In the other word, the energy barrier for zinc corrosion in 2M HCl solution in the presence of the used complexes is greater than in the presence of thiourea or ligands. This case was simply indicates to, the corrosion rate in the presence of complexes is lower than in the presence of thiourea or ligands. Generally, E_a values of the all tested inhibitors decrease in the order, complex $[C_{16}H_{16}Cl_2CON_2O_6S] > [C_{16}H_{32}N_4O_{13}(CO)_2] >$ thiourea $> [C_9H_{12}N_2O_4S] > [C_{13}H_{16}N_4]$, which reflect their tendency to inhibit the corrosion of zinc in 2M HCl solution.

CONCLUSION

The following conclusions can be drawn from this work:

1. The all used inhibitors give inhibiting action at low concentrations and they reveal missing of inhibition efficiency at relatively higher concentrations.
2. The inhibition efficiency and the promotion action increase with increasing the concentrations of the tested inhibitors in the concentrations range of inhibition and missing inhibition action respectively.
3. The adsorption of the tested inhibitors on zinc surface obeyed langmuir's adsorption isotherm.
4. All the used inhibitors provides protection through a physisorption process.
5. The results show that the used complexes are superior inhibitors than thiourea and the used ligands on zinc surface in 2M HCl solution.
6. Some inhibitors act as promotion for metal. This case may be related to their reduction potentials at definite concentration attain more positive values than the reduction potential of metal, and hence accelerate the metal anodic dissolution.

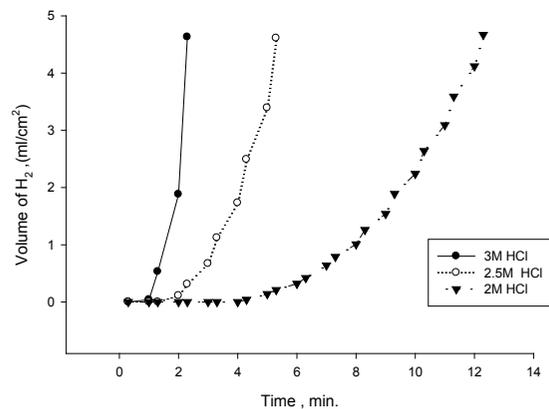


Fig.(1):Volume of H₂ gas evolved (ml/ cm²) as a function of time for the reaction of Zinc in HCl solution of different concentrations at 30°C°

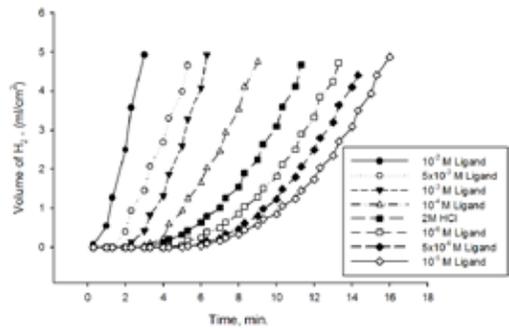


Fig.(2):Volume of H₂ gas evolved (ml/ cm²) as a function of time for the reaction of Zinc in 2M HCl solution in absence and presence different concentrations of ligand (C₁₃H₁₆N₄) at 30°C°.

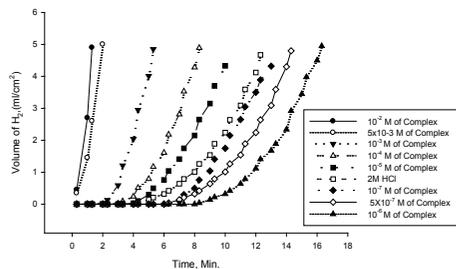


Fig.(3): Volume of H₂ gas evolved (ml/ cm²) as a function of time for the reaction of Zinc in 2M HCl solution in absence and presence different concentrations of Complex (C₉H₁₆Cl₂CoN₂O₆S) at 30°C°

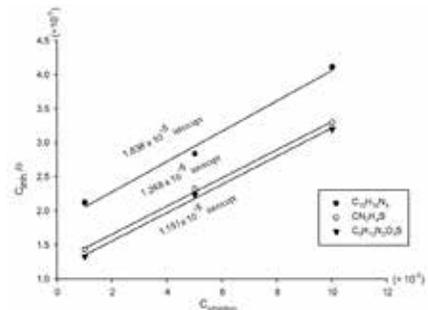


Fig.(4):Langmuir adsorption isotherm for corrosion of Zinc in 2M HCl solution in presence the used ligands at the concentrations range of the corrosion inhibition at 30°C°

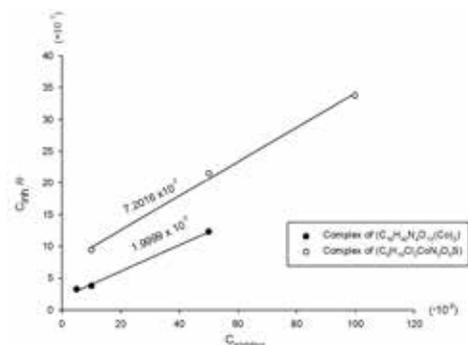


Fig.(5): Langmuir adsorption isotherm for corrosion of Zinc in 2M HCl in presence the used complexes at concentrations range of corrosion inhibition at 30°C°.

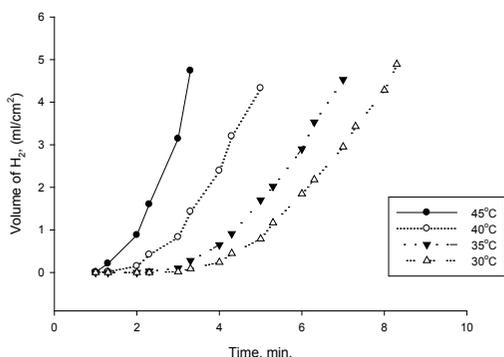


Fig.(6): Volume of gas evolved (ml/ cm²) as a function of time for the reaction of Zinc in 2M HCl solution in presence 5x10⁻⁷ M of Complex (C₉H₁₆Cl₂CoN₂O₆S) at different temperatures.

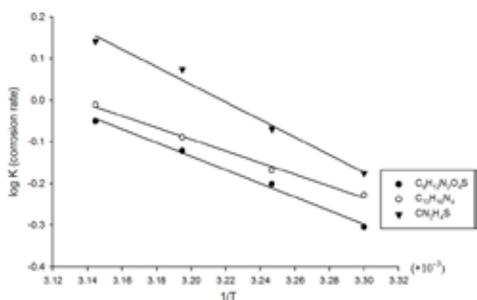


Fig.(7): Arrhenius plots of logarithm corrosion rate versus 1/T for corrosion of Zinc in 2M HCl in presence 5x 10⁻⁶ M of the used ligands.

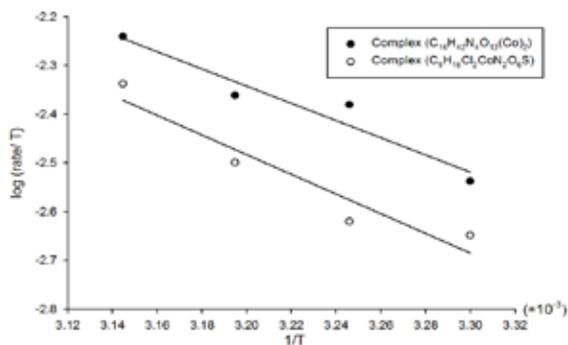


Fig.(8): Arrhenius plots of logarithm(corrosion rate /T) versus 1/T for corrosion of Zinc in 2M HCl in presence 5x 10⁻⁷ M of the used complexes.

Table (1): The corrosion rate, A, the surface coverage, θ , The inhibition efficiency, I, and the values of $C_{inh.} / \theta$, for different concentrations of thiourea and ligands, in the range of inhibition action by using gasometric technique at 30 C°.

Concentration of inhibitors (M)	log C _{inh.}	thiourea (CN ₂ H ₄ S)			Ligand (C ₁₃ H ₁₆ N ₄)			Ligand (C ₉ H ₁₆ Cl ₂ CoN ₂ O ₆ S)		
		A	θ	I	A	θ	I	A	θ	I
		$C_{inh.} / \theta$			$C_{inh.} / \theta$			$C_{inh.} / \theta$		

1x10 ⁻⁶	-6.0	0.3283904	0.06971556	6.971556	1.4344x10 ⁻⁵	0.336378849	0.047085412	4.7085412	2.1238x10 ⁻⁵	0.336438675	0.075244544	7.5244544	1.3290x10 ⁻⁵
5x10 ⁻⁶	-5.3	0.2769	0.215580736	21.558	2.31931x10 ⁻⁵	0.2908	0.17620396	17.62039	2.8376x10 ⁻⁵	0.274205357	0.22321428	22.3214285	2.240x10 ⁻⁵
1x10 ⁻⁵	-5.0	0.246030303	0.303030303	30.30	3.30x10 ⁻⁵	0.267201687	0.243054711	24.3054	4.1143x10 ⁻⁵	0.2426875	0.3125	31.25	3.20x10 ⁻⁵

Table (2): The corrosion rate, A, the surface coverage, θ , The inhibition efficiency, I, and the values of $C_{inh.} / \theta$, for different concentrations of complexes; in the range of inhibition action by using gasometric technique at 30 C°.

Concentration of inhibitors (M)	log C _{inh.}	Complex of (C ₉ H ₁₆ Cl ₂ CoN ₂ O ₆ S)				Complex of (C ₁₃ H ₁₆ N ₄ O ₁₃ (Co) ₂)			
		A	θ	I	$C_{inh.} / \theta$	A	θ	I	$C_{inh.} / \theta$
5x10 ⁻⁸	-7.3	-	-	-	-	0.2987	0.15382	15.38	3.25x10 ⁷
1x10 ⁻⁷	-7.0	0.3156	0.10594	10.59	9.43x10 ⁻⁷	0.2604	0.26232	26.23	3.81x10 ⁷
5x10 ⁻⁷	-6.3	0.27106	0.23213	23.21	21.54x10 ⁻⁷	0.2098	0.40566	40.57	12.32x10 ⁷
1x10 ⁻⁶	-6.0	0.2486	0.2957	29.58	33.81x10 ⁻⁷	-	-	-	-

Table (3): Activation thermodynamic parameters E_a, ΔH , ΔS and ΔG_{ads} for Zinc in 2 M HCl with absence and presence 5x10⁻⁶ M thiourea , ligands and 5x10⁻⁷ M complexes .

Corrosive media	E _a ,KJ/mol	- ΔH ,KJ/mol	- ΔS , J/mol K°	- ΔG_{ads} ,KJ/mol
Blank +Ligand (C ₉ H ₁₆ N ₄ O ₆ S)	31.321	28.738	245	38.19
Blank +Ligand (C ₁₃ H ₁₆ N ₄)	29.442	26.844	245.033	37.614
Blank +Ligand thiourea (CN ₂ H ₄ S)	40.301	37.692	242.52	38.59
Blank + Complex of (C ₁₆ H ₄₂ N ₄ O ₁₃ (Co) ₂)	55.991	36.632	239.68	49.032
Blank + Complex of (C ₉ H ₁₆ Cl ₂ CoN ₂ O ₆ S)	58.632	38.26	242.304	45.781

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