

# Absence and presence Organic and Inorganic Inhibitors

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## Abstract

The aggressive effect of different concentrations of HNO<sub>3</sub> and the inhibitive action of some organic and inorganic additives on the corrosion of copper metal have been studied by thermometric technique. The rate of metal dissolution increases with acid concentration. The copper dissolution rate in 2M HNO<sub>3</sub> was dependent on the chemical properties and concentration of the used additives. The inhibitive action of these compounds obey the Langmuir adsorption isotherm. The degree of surface coverage ( $\theta$ ) of adsorbed organic and inorganic additives was determined from the reaction number (R.N.) values. The thermodynamic parameters  $K_{ads}$  and  $\Delta G_{ads}^{\circ}$  of organic additives are calculated and illustrated. The values of  $\Delta G_{ads}^{\circ}$  clear strong physisorption of the tested organic inhibitors on copper metal surface.

**Keywords:** Copper; Acid Corrosion; Passivity; Thermometry.

## Introduction

Corrosion is a problem of great economic importance to industry and, hence, it is an important area of research. Copper has been widely used for many applications including automotive and electronic industries. However, it corrodes in aggressive media such as O<sub>2</sub>, H<sup>+</sup> and Cl<sup>-</sup>. The corrosion inhibition of metals by organic and inorganic compounds results from the adsorption of molecules at the surface of metal. The extent of adsorption of an inhibitor depends on many factors<sup>(1)</sup>: the nature and the surface charge of the metal; the mode of adsorption of the inhibitor; the inhibitor's chemical structure; and the type of the aggressive solution. The presence of hetero-atoms (such as: oxygen, nitrogen, sulfur, phosphorus), triple bonds, and aromatic rings in the inhibitor's chemical structure enhance the adsorption process<sup>(2)</sup>. It has been reported that the inhibitor efficiency (%) of heterocyclic organic compounds follows the sequence: oxygen < nitrogen < sulfur < phosphorus<sup>(3,4)</sup>. The aim of the present study reports on the corrosion of copper in HNO<sub>3</sub> solutions. Special attention is paid to the effect of acid concentration and the presence of several organic and inorganic additives. Because the reaction between copper and HNO<sub>3</sub> solution is highly exothermic, the Mylius<sup>(5)</sup> thermometric corrosion test is used. The present work also evaluates the efficiencies of some simple, cheap and available; organic nitrogen compounds, containing in their structures either oxygen or sulfur atoms, such as phenylhydrazine, urea, thiourea, N-allylthiourea, and thiosemicarbazide and inorganic compounds, such as: Na<sub>2</sub>CrO<sub>4</sub>, Na<sub>2</sub>WO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> as corrosion inhibitors for copper in 2M HNO<sub>3</sub> solution. The thermodynamic adsorption parameters such as the standard free energy of adsorption in presence of organic inhibitors are calculated. The inhibition performance is evaluated by thermometry measurements.

## Experimental

### Material and Sample Preparation:

The copper sample with a purity of 99.99% were cut from a piece of copper plate. The surface area of each sample equals 1.0 cm<sup>2</sup>. Each new sample surface was polished prior to any experiment with 800 grit SiC paper, rinsed with distilled water and polished with an acetone-saturated paper towel to remove any grease and produce a relatively scratch free, smooth, shiny surface. It was then rinsed with triply distilled water<sup>(6)</sup>.

### The Electrolyte Media:

All chemicals were of analytical grade. Bi-distilled water was used to prepare a mother solution of 4M HNO<sub>3</sub>. The molarities are determined by titration against a standard NaOH solution using methyl orange as indicator. Difference concentrations of HNO<sub>3</sub> were prepared by dilution from a concentrated mother solution. Difference concentrations of organic and inorganic inhibitors were prepared by dissolving the calculated weight of each concentration in 100 ml of 2M HNO<sub>3</sub>.

### The Electrolytic Cell and Thermometry Measurements:

The thermometric vessel used is made of pyrex glass (Mylius tube) kept inside a Dewar's flask to minimize heat exchange with the surrounding<sup>(7)</sup>. The clean Cu samples were immersed in 100 ml of the corroding solution inside the Mylius tube<sup>(5)</sup> and the variation of temperature was followed with time using a calibrated thermometer. The reaction number (R. N.) is calculated from<sup>(8)</sup>,

$$R.N. = \frac{T_{\max.} - T_{\text{initial}}}{t} \text{ } ^\circ\text{C min}^{-1} \quad (1)$$

where  $T_{\max.}$  and  $T_{\text{initial}}$  are the maximum and initial solution temperatures, respectively, and  $t$  is the time in minutes taken to reach the maximum temperature,  $T_{\max.}$ . The reaction number (R.N.) is proportional to the rate of corrosion of copper. Several sets of experiments are carried out. In one set, the copper sample of, specified surface area, are made to react with a constant volume (100 ml) of  $\text{HNO}_3$  solutions of different concentrations. In another set of experiments, the effect of addition of increasing concentrations of organic compounds such as, phenylhydrazine, urea, thiourea, N-allylthiourea, thiosemicarbazide and inorganic salts such as  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{WO}_4$ , and  $\text{Na}_2\text{HPO}_4$  on the dissolution of copper in 2M  $\text{HNO}_3$  is also examined.

### Results and discussion

Figure (1) shows a relation between the solution temperature versus time, minute, for the reaction between Cu of specified surface area and 100 ml  $\text{HNO}_3$  solution of different concentrations. It is essential to note that the curves of the reactions between copper and  $\text{HNO}_3$  increase steadily and rapidly with time to attain a maximum value,  $T_{\max.}$ , in the concentration range from 1 to 4M. However, the curves of the reactions in concentrations lower than 1M increase slowly to attain  $T_{\max.}$ . It was shown also that  $T_{\max.}$  of all curves increases with increasing the acid concentrations. These cases were simply related to the quantity of heat evolved from the reaction increases with increasing nitric acid concentration.  $T_{\max.}$  declines again slowly with time in the concentrations up to 1M and in concentrations lower than 1M attains without declines again, this is due to the presence and absence passive film on copper surface respectively.

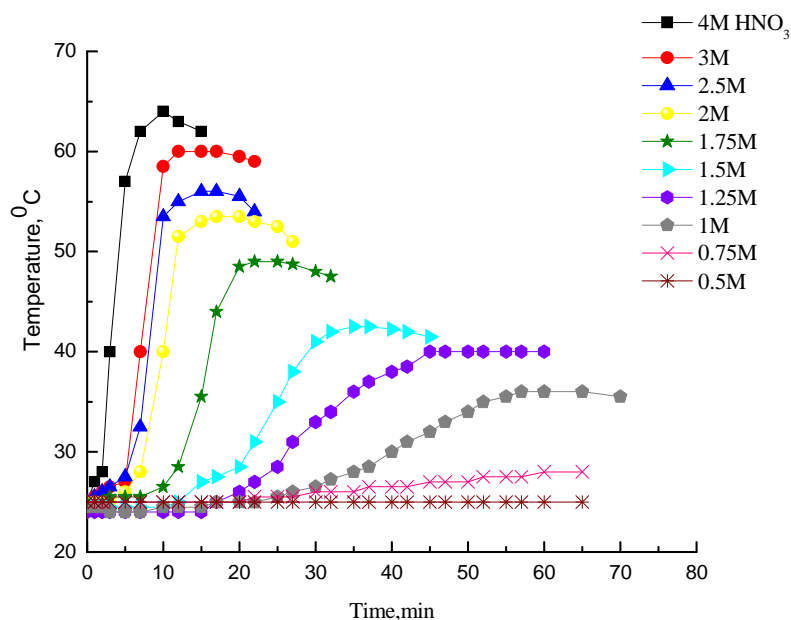


Fig. (1): Temperature - time curves for the reaction between Cu and  $\text{HNO}_3$  solutions of different concentrations.

Figure (2) displays the variation of  $\Delta T$ , i. e.  $(T_{\max} - T_{\text{initial}})$ , as a function of acid molarity. It was shown that  $\Delta T$  increases with increasing the concentration of nitric acid. This case was simply related to the reaction between copper and  $\text{HNO}_3$  solution is highly exothermic<sup>(5)</sup>.

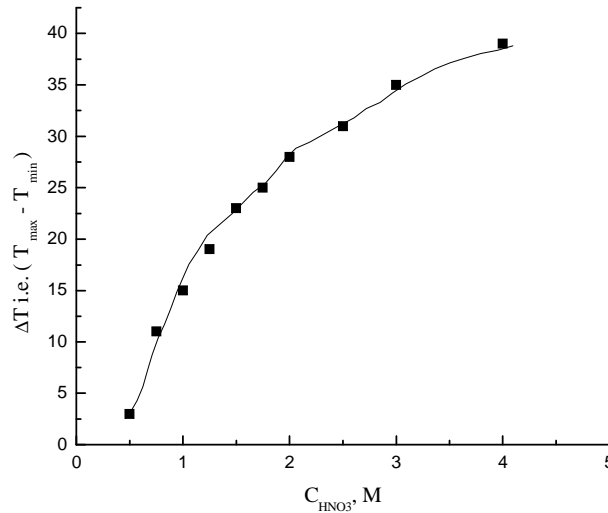


Fig. (2): Variation of  $\Delta T$ , i.e.  $(T_{\max} - T_{\min})$  of system with the concentrations of  $\text{HNO}_3$ .

Figure (3) offers the variation of  $\ln R.N.$ ,  $^{\circ}\text{C min}^{-1}$ , of Cu dissolution as a function of  $\ln C$ , M of  $\text{HNO}_3$ , according to the following relation<sup>(7)</sup>;

$$\ln R.N. = k - n \ln C_{\text{inh.}} \quad (2)$$

where  $k$  and  $n$  are constants. It reveals that the rate of copper corrosion, i. e.  $R.N.$ , in  $\text{HNO}_3$  solution enhances with increasing the acid concentrations. This case was simply related to the reaction rate depends on the reactants concentration.

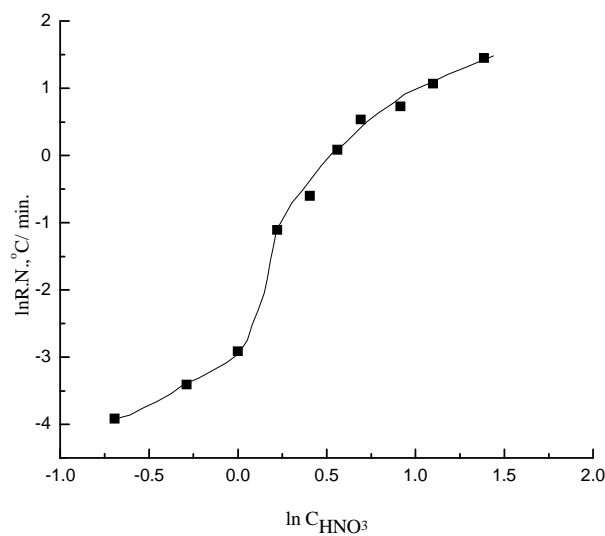


Fig. (3): Variation of  $\ln(R.N.)$  of copper dissolution with  $\ln$  of different concentrations of nitric acid.

Figures (4, 5) represent the variation of solution temperature with time for the dissolution of Cu in 2M HNO<sub>3</sub> in absence and presence of different concentrations of urea and Na<sub>2</sub>CrO<sub>4</sub>. Similar curves are obtained for the other additives (not shown). It is essential to note from these figures and the like that the maximum temperature (T<sub>max</sub>) and the time (t) decreases and increases respectively with increasing the concentrations of organic and inorganic additives in 2M HNO<sub>3</sub>. This is due to the enhancement of the inhibition efficiency of each additive with increasing its concentration.

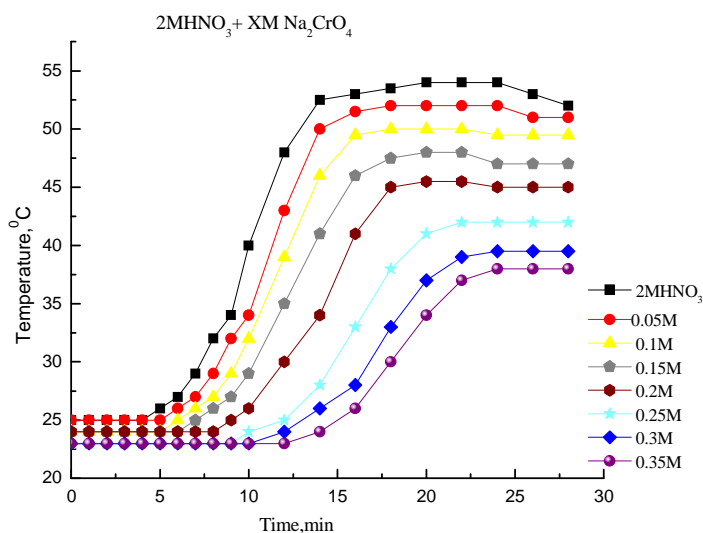


Fig.(4): Temperature - time curves for dissolution of Cu in 2M HNO<sub>3</sub> in absence and presence of different concentrations of Na<sub>2</sub>CrO<sub>4</sub>.

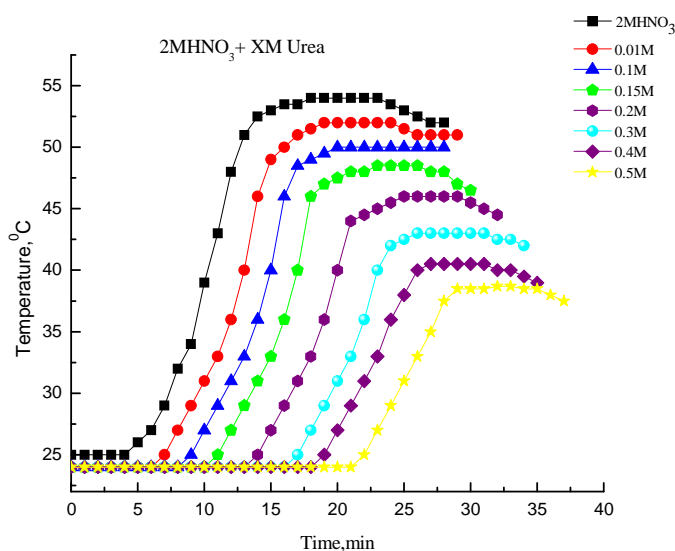


Fig.(5): Temperature - time curves for dissolution of Cu in 2M HNO<sub>3</sub> in absence and presence of different concentrations of urea.

Figures (6, 7) display the variation of  $\ln R.N., ^\circ C \text{ min}^{-1}$  of Cu dissolution in 2M HNO<sub>3</sub> as a function of  $\ln C, M$  of organic and inorganic inhibitors according to equation (2). The curves of figures (6, 7) reveal that the R.N. of copper dissolution in 2M HNO<sub>3</sub> depends on the concentrations and type of the additive inhibitors.

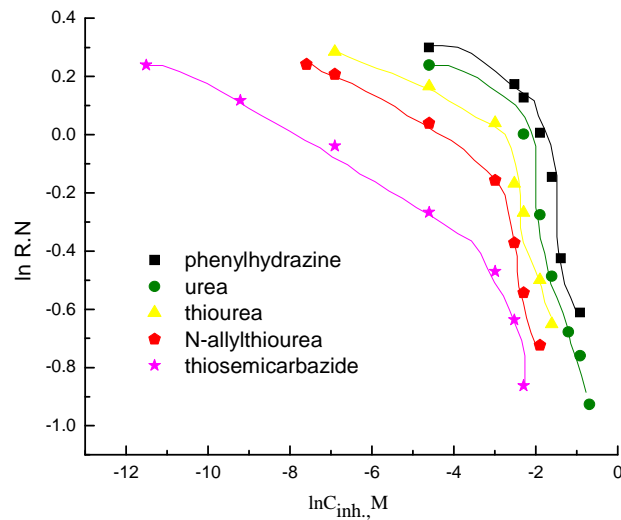


Fig.(6): Variation of ln R. N. of Cu dissolution in 2M HNO<sub>3</sub> with ln different concentrations of organic inhibitors.

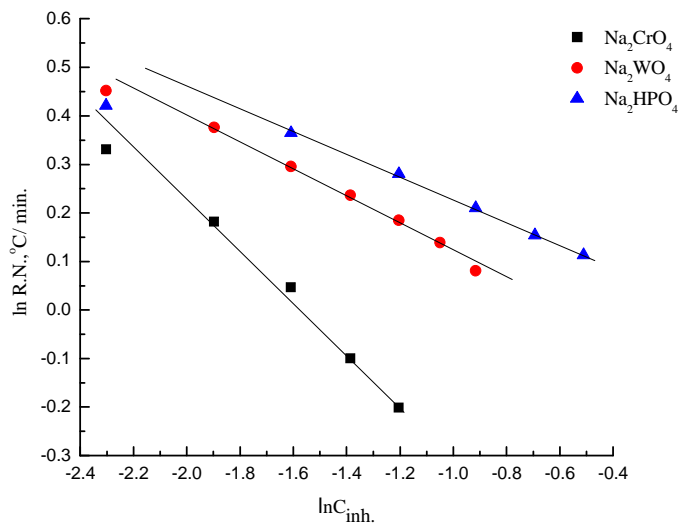


Fig.(7) :- Variation of ln R.N.of Cu dissolution in 2M HNO<sub>3</sub> with ln different concentrations of inorganic inhibitors.

Figures (8, 9) represent the percentage variation in the reaction number, %R.N., for Cu dissolution in 2M HNO<sub>3</sub> solution as a function of the logarithm of the molar concentrations of organic and inorganic inhibitors. The percentage variation calculated from the following relation<sup>(8, 9)</sup>;

$$\% \text{variation in R.N.} = \frac{[(R.N.)_{\text{free}} - (R.N.)_{\text{add}}]}{(R.N.)_{\text{free}}} \times 100 \quad (3)$$

As can be seen from the curves of figures (8, 9), the corrosion reaction of copper decreases with increasing the organic and inorganic additives.

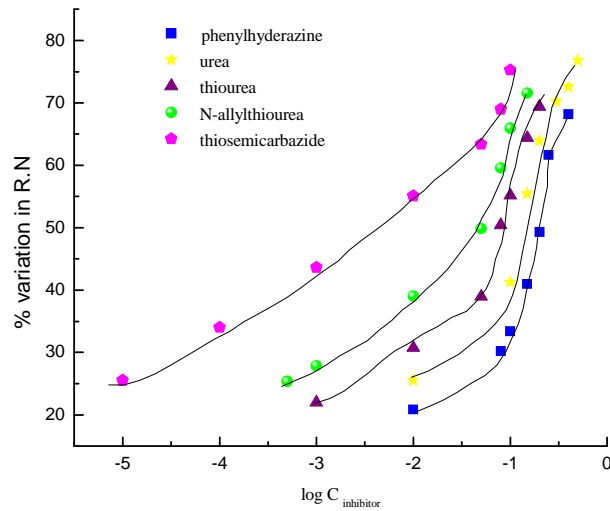


Fig.(8) Percentage variation in reaction number, %R.N., for Cu dissolution in 2M HNO<sub>3</sub> solution as a function of logarithm of molar concentrations of organic inhibitors.

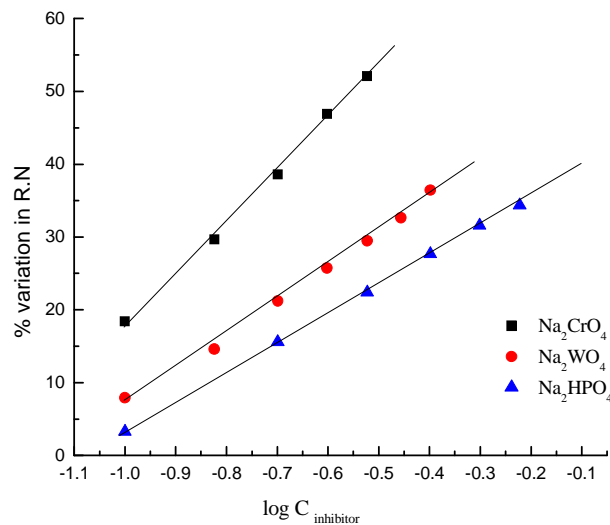


Fig.(9) Percentage variation in reaction number, %R.N., for Cu dissolution in 2M HNO<sub>3</sub> solution as a function of logarithm of molar concentrations of inorganic inhibitors.

Figure (8) shows a drop in the rate of corrosion with increasing the organic additives concentration, which depends on the type of added ions. The inhibition of organic additives decrease in the order: thiosemicarbazide > N-allylthiourea > thiourea > urea > phenylhydrazine.

Figure (9) clears that the inhibition of inorganic additives decreases in the order: Na<sub>2</sub>CrO<sub>4</sub> > Na<sub>2</sub>WO<sub>4</sub> > Na<sub>2</sub>HPO<sub>4</sub>. The inhibiting action of organic and inorganic additives at the all concentration is assumed to be due to the adsorption on the active site of copper surface. The surface coverage,  $\theta$ , which represents the part of the surface covered by the inhibitor molecules and the percentage inhibition efficiency, I, for the different additives are calculated from the following relations<sup>(7)</sup>,

$$\Theta = 1 - (R.N.)_{add.} / (R.N.)_{free} \quad (4)$$

$$I = [1 - (R.N.)_{add.} / (R.N.)_{free}] \times 100 \quad (5)$$

where  $(R.N.)_{add.}$  and  $(R.N.)_{free}$  are the reaction numbers in presence and absence of organic and inorganic additives. The values of surface coverage ( $\theta$ ) and the percentage inhibition efficiency (I) for different inorganic and organic additives concentrations are listed in Table (1, 2).

Table (1) The surface coverage,  $\theta$ , and the percentage inhibition efficiency, I, for different concentrations of inorganic inhibitors by using thermometric technique.

concentrations	$Na_2CrO_4$		$Na_2WO_4$		$Na_2HPO_4$	
	$\theta$	I	$\theta$	I	$\theta$	I
0.1M	0.184	18.4	0.079	7.9	0.033	3.3
0.15M	0.296	29.6	0.146	14.6	0.107	10.7
0.2M	0.385	38.5	0.212	21.2	0.168	16.8
0.25M	0.469	46.9	0.257	25.7	0.194	19.4
0.3M	0.529	52.9	0.295	29.5	0.224	22.4
0.35M	-	-	0.327	32.7	0.255	25.5
0.4M	-	-	0.364	36.4	-	-
0.45M	-	-	-	-	-	-
0.5M	-	-	-	-	-	-
0.55M	-	-	-	-	0.316	31.6
0.6M	-	-	-	-	0.379	37.9

Table(2) The surface coverage,  $\theta$ , and the percentage inhibition efficiency, I, for different concentrations of organic inhibitors by using thermometric technique.

contractions	Phenyl hydrazine		urea		Thiourea		N-allylthiourea		Thiosemi-carbazide	
	$\theta$	I	$\theta$	I	$\theta$	I	$\theta$	I	$\theta$	I
$1 \times 10^{-5} \text{ M}$	-	-	-	-	-	-	-	-	0.265	25.6
$1 \times 10^{-4} \text{ M}$	-	-	-	-	-	-	-	-	0.341	34.1
$5 \times 10^{-4} \text{ M}$	-	-	-	-	-	-	0.256	25.6	-	-
$1 \times 10^{-3} \text{ M}$	-	-	-	-	0.220	22	0.279	27.9	0.436	43.6
$5 \times 10^{-3} \text{ M}$	-	-	-	-	-	-	-	-	-	-
$1 \times 10^{-2} \text{ M}$	0.208	20.8	0.250	25	0.308	30.8	0.391	39.1	0.551	55.1
$5 \times 10^{-2} \text{ M}$	-	-	-	-	0.389	38.9	0.498	49.8	0.634	63.4
$8 \times 10^{-2} \text{ M}$	0.302	30.2	-	-	0.504	50.4	0.596	59.6	0.689	68.9
$1 \times 10^{-1} \text{ M}$	0.33	33	0.423	42.3	0.552	55.2	0.669	66.9	0.753	75.3
0.15M	0.401	40.1	0.555	55.5	0.644	64.4	0.716	71.6	-	-
0.2M	0.493	49.3	0.639	63.9	0.694	69.4	-	-	-	-
0.25	0.612	61.2	-	-	-	-	-	-	-	-
0.3M	-	-	0.702	70.2	-	-	-	-	-	-
0.35M	-	-	-	-	-	-	-	-	-	-
0.4M	0.682	68.2	0.726	72.6	-	-	-	-	-	-
0.45M	-	-	0.768	76.8	-	-	-	-	-	-

Figures (1-9) and Tables (1, 2) reveal the following conclusions to be drawn:

- 1 – All tested organic and inorganic additives cause inhibition against the corrosion of copper in 2M  $\text{HNO}_3$  solutions.
- 2 – The percentage inhibition efficiency (I) of these compounds increases with increasing their concentration and depends on additive type.
- 3 – The inhibition efficiency of organic inhibitors is major than inorganic against the corrosion of copper in 2M  $\text{HNO}_3$ .
- 4 – In the presence of one and the same concentration of organic additives, the percentage inhibition efficiency (I) decreases in the order: thiosemicarbazide > N-allylthiourea > thiourea > urea > phenylhydrazine. In like manner the inhibition efficiency of inorganic inhibitors decreases in the order:  $\text{Na}_2\text{CrO}_4 > \text{Na}_2\text{WO}_4 > \text{Na}_2\text{HPO}_4$ .

Figure (10) represents the langmuir adsorption isotherm ( $C_{\text{inh.}}, \text{M}/\theta$  versus  $C_{\text{inh.}}, \text{M}$ ) of organic inhibitors in 2M  $\text{HNO}_3$ . It is essential to note from this figure that the experimental data obtained from thermometry measurements could fit the langmuir's adsorption isotherm.



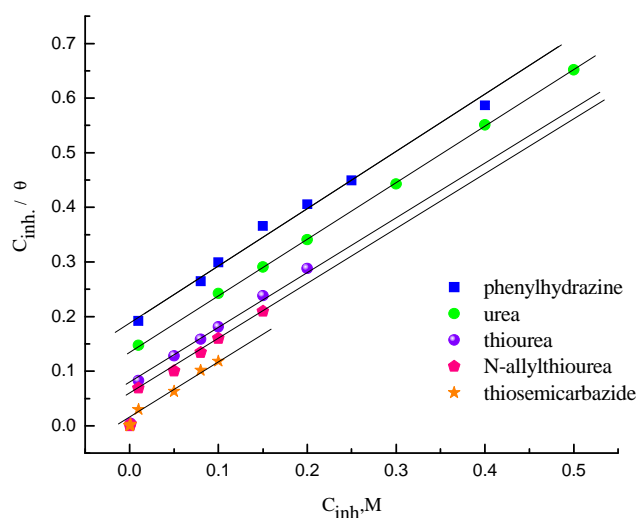


Fig.(10): langmuir adsorption isotherm ( $C_{inh.}/\theta$  v.s. $C_{inh.}$ ) of the used inhibitors in 2M  $HNO_3$ .

According to this isotherm, the surface coverage ( $\theta$ ) is related to inhibitor concentration,  $C_{inh.}$ , as the following relation<sup>(7, 10)</sup>,

$$C_{inh.}/\theta = 1/K_{ads.} + C_{inh.} \quad (6)$$

where  $K_{ads.}$  is the equilibrium constant of the adsorption process, and  $C_{inh.}$  is the inhibitor concentration. Straight lines are obtained when  $C_{inh.}/\theta$  is plotted versus  $C_{inh.}$  for all tested organic inhibitors. The slopes of organic inhibitors curves are nearly the same and very close to 1 as seen in figure (10). The values of  $K_{ads.}$  can be calculated from the intercepts of the straight lines of figure (10).  $K_{ads.}$  is related to the standard free energy of reaction ( $\Delta G^{\circ}_{ads.}$ ) in  $kJ\ mol^{-1}$ , with the following equation<sup>(11)</sup>;

$$K_{ads.} = 1/55.5 \cdot e^{-\Delta G^{\circ}_{ads.}/RT} \quad (7)$$

where 55.5 is the concentration of water in the solution in mol/L, R is the general gas constant in  $J\ mol^{-1}\ deg^{-1}$  and T is the absolute temperature. The values of  $K_{ads.}$  and the standard free energy of the reaction ( $\Delta G^{\circ}_{ads.}$ ) are given in Table (3).

Table (3) represent equilibrium constant,  $K_{ads.}$ , and the free energy of adsorption,  $-\Delta G_{ads.}$ , of organic Inhibitors for Cu in 2M  $HNO_3$  solution at 25 °C .

Inhibitor	$K_{ads.}, mol^{-1}$	$-\Delta G^{\circ}_{ads.}, kJ\ mol^{-1}$
Phenylhydrazine	7.14	14.82
Urea	11.98	16.10
Thiourea	32.57	18.58
N-allylthiourea	80.77	20.83
Thiosemicarbazide	294.11	24.03

Generally, if the values of  $\Delta G^{\circ}_{ads.}$  are in the range up to  $-20\ kJ/mol$ , they are consistent with physisorption of the organic molecules or their protonated species on the surface. Inhibition is therefore, due to electrostatic interaction between charged species and the charged metal, while those above  $-40\ kJ/mol$  are associated with chemisorption as a result of sharing or transfer of electrons from organic species to the metal surface to form a metal bond<sup>(12,13)</sup>. The calculated values of the standard free energy ( $\Delta G^{\circ}_{ads.}$ ) of the tested organic additives vary between  $14.82\ kJ\ mol^{-1}$  and  $24.03\ kJ\ mol^{-1}$ . This case was simply related to the adsorption mechanism of all the used organic inhibitors on copper in 2M  $HNO_3$  solution is through physisorption. The values of  $\Delta G^{\circ}_{ads.}$  of the tested organic inhibitors decrease in the order, thiosemicarbazide > N-allylthiourea > thiourea > urea > phenylhydrazine, which reflect their tendency to inhibit the corrosion of copper in 2M  $HNO_3$  solutions.

## Conclusions

The following conclusions can be drawn from this work:

- 1- The tested organic and inorganic additives cause a decrease in the rate of corrosion of copper in 2M HNO<sub>3</sub> by a way of a physisorption on its surface.
- 2- The rate of oxide film destruction in presence of these additives decreases with increasing their concentration and depends on inhibitor type.
- 3- In presence of one and the same concentration of organic and inorganic additives, the inhibition efficiency (I) decreases in the order: thiosemi-carbazide > N-allylthiourea > thiourea > urea > phenylhydrazine and NaCrO<sub>4</sub> > Na<sub>2</sub>WO<sub>4</sub> > Na<sub>2</sub>HPO<sub>4</sub> respectively.
- 4- The inhibition efficiency of the all tested organic compounds is major than the all tested inorganic compounds against corrosion of copper in 2M HNO<sub>3</sub> solutions.
- 5- The calculated standard free energy ( $\Delta G^{\circ}_{ads}$ ) of reaction in presence organic additives reveals strong physisorption process.

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