"Corrosion Inhibition of Copper by Some Thiourea Derivatives"

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Abstract

The effect of some thiourea derivatives on the corrosion inhibition of copper has been investigated in 2mol dm^{-3} HNO_3 solution. Weight-loss and polarization measurements were applied to analyse the metal corrosion behaviour in the absence and presence of the inhibitor. The results show that all the studied thiourea derivatives inhibit the corrosion of copper in the solution and that the inhibiting efficiency increases with a decrease in temperature or an increase in concentration of the thiourea derivatives. The obtained results show that the adsorption of the additives used follow the Temkin adsorption isotherm. Moreover, the thermodynamic activation parameters of the copper corrosion reaction were calculated and discussed.

Key words: Corrosion inhibitor, thiourea derivatives, nitric acid, copper.

Introduction

Most organic substances employed as corrosion inhibitors protect the metal by forming a chelate on the metal surface$^{(1)}$. The efficiency of the inhibitor depends on the stability of the chelate formed$^{(2)}$. The effectiveness of an inhibitor depends on the type and the nature of the substituents present in the inhibitor molecule$^{(3)}$. The inhibitor molecule should have centers capable of forming bonds with the metal surface by

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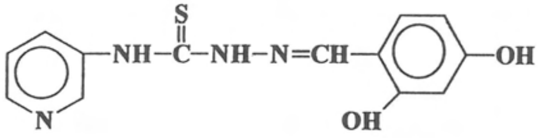
electron transfer, in which the metal acts as an electrophile and the inhibitor acts as a Lewis base whose nucleophilic centers are O and/or N atoms with free electronic pairs which are readily available for sharing.

Thiourea has been repeatedly recommended as inhibitor for the dissolution of metals in acid solutions, either alone(4-12) or in combination with other additives(13-18). It uses as restrainer in descaling and pickling baths has also been reported(19-23).

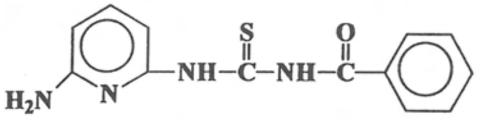
The present work aims to characterize the effect of the following thiourea derivatives as corrosion inhibitors of copper in nitric acid solution, using weight-loss and polarization measurements.

The thiourea derivatives are:

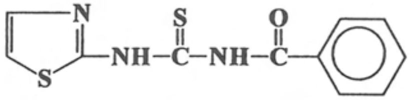
I) 4(3-pyridyl)-1-(2,4-dihydroxy benzaldehyde)3-thiosemicarbazone.



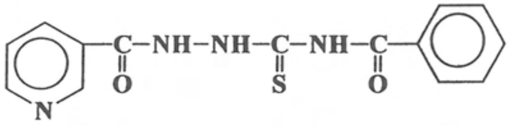
II) N(6-amino-pyridyl)N`-benzoyl thiourea.



III) N-thiazole-N`-benzoyl thiourea

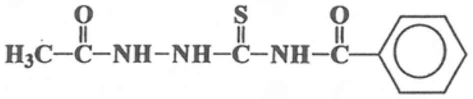


(V) N-isonicotinamido-N-benzoyl thiourea

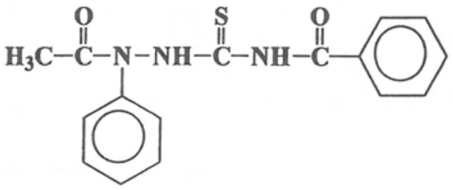


V) N-amino-N`-nicotinamido thiourea

VI) N-acetamido-N`-benzoyl thiourea



VII) N-(N-phenylacetamido)-N`-benzoyl thiourea



Experimental

Copper strips of 1.6 cm^3 size were used for weight-loss measurements. For galvanostatic studies, a cylindrical rod embedded in araldite with an exposed surface area of 1 cm^2 was used. The electrodes were polished with different grades of emery paper, degreased with acetone and rinsed with distilled water. AR grade nitric acid was used for preparing solutions. The composition of copper electrodes was given as shown in table 1.

Table 1.

Element	P	Cd	S	Zn	Pb	Cu
Weight,%	0.0015	0.003	0.0015	0.0005	0.001	rest

Weight loss measurements were carried out as described elsewhere(24). Galvanostatic polarization studies was carried out using Amel Model 549 potentiostat / Galvanostat.

The electrode potential was measured against a saturated calomel electrode (SCE). A platinum wire was used as an auxiliary electrode.

Results and Discussion

Weight loss measurements

Table 2 gives values of the inhibition efficiency obtained from the weight loss measurements of copper for different concentrations of tested thiourea derivatives in 2mol dm^{-3} HNO_3 at 30±C after 100 minutes. of immersion. The inhibition efficiency is defined as follows:

$$(\eta)\ \% = [(Wo - W) / Wo\ ] \times 100 \qquad (1)$$

where W_o and W are the values of weight loss of copper after immersion in solutions without and with inhibitor, respectively.

All tested thiourea derivatives inhibit the corrosion of copper and the inhibition efficiency increases with the increasing inhibitor concentration in the test concentration.

The order of inhibition efficiency of the additive compounds over most of the concentration range is: II > III > V > VI > I > IV > VII.

Table (2).Effect of the additive concentration on the inhibition efficiency for copper in 2 mol dm^{-3} HNO_3 after 100 minutes.

Conc. In mol dm^{-3}	% Inhibition (η)						
	I	II	III	IV	V	VI	VII
5.0×10^{-5}	53.2	81.2	74.9	48.5	70.4	56.3	39.1
1.0×10^{-4}	60.9	86.0	79.2	59.4	75.0	64.8	53.1
2.0×10^{-4}	69.5	88.2	84.4	67.2	79.6	72.8	62.4
4.0×10^{-4}	77.0	89.9	87.4	75.0	82.9	80.5	70.3
6.0×10^{-4}	85.1	92.2	89.9	79.4	86.2	85.1	78.1
8.0×10^{-4}	93.0	94.0	93.9	85.2	89.2	88.8	83.6

Polarization measurements

The cathodic polarization curves for copper in 2 mol dm^{-3} HNO_3 at various concentrations of compound II is shown in Fig. 1. It is clear that the cathodic reaction (hydrogen evolution) is inhibited and the inhibition increases along with the inhibitor concentration. Tafel lines of nearly equal slopes were obtained. The constancy of this cathodic slope can indicate that the mechanism of proton discharge reaction does not change by addition of the thiourea derivatives to the acidic medium.

Values of corrosion current density ($I_{corr.}$), corrosion potential ($E_{corr.}$), cathodic Tafel slope (b_c) and corrosion inhibition (η%) for different concentrations of compound II are given in table 3.

The inhibition efficiency is defined as

$$\eta(\%) = \frac{I_{corr.} - I_{corr.(inh.)}}{I_{corr.}} \qquad (2)$$

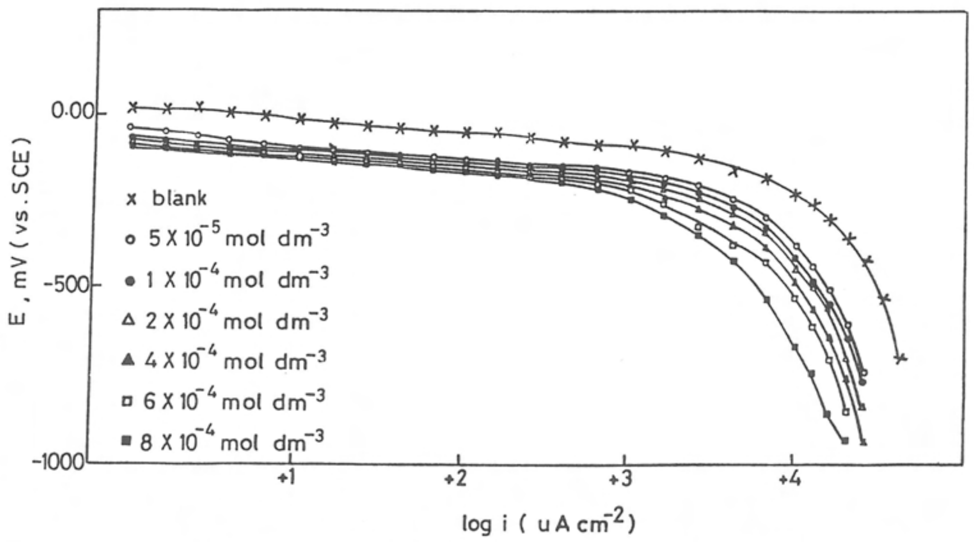


Fig. 1. Cathodic polarization curves for copper in 2 mol dm^{-3} HNO_3 in absence and in presence of different concentrations of compound II at 25°C.

where $I_{corr.}$ and $I_{corr.(inh.)}$ are the corrosion current density values without and with inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential. From this result, it can be concluded that:

Table (3). Effect of compound II concentration on the free corrosion potential, corrosion current density, percentage protection, Tafel slope and surface coverage(θ) for copper in 2 mol dm^{-3} HNO_3 at 25°C.

Concentration mol dm^{-3}	E_{corr} (mV)	I_{corr} ($\mu A\ cm^{-2}$)	%η	Tafel slope b_c(mV dec^{-1})	θ
0.0	+20	2290.8		312	
$5.0 x10^{-5}$	-37	616.5	73.1	314	0.73
$1.0 x10^{-4}$	-62	380.1	83.4	312	0.83
$2.0 x10^{-4}$	-68	301.9	86.8	312	0.87
$4.0 x10^{-4}$	-75	229.0	90.0	311	0.90
$6.0 x10^{-4}$	-80	144.5	93.7	312	0.94
$8.0x10^{-4}$	-90	109.6	95.2	312	0.95

- The values of corrosion current density ($I_{corr.}$) of copper in the inhibited solution were smaller than those for the inhibitor - free solution.
- $I_{corr.}$ decreases with increasing inhibitor concentration and addition of thiourea derivatives does not change the values of b_c.
- The results of inhibition efficiency obtained from the polarization curves correspond to those from the corrosion weight loss.
- The concentration of the additives influences the free corrosion potential ($E_{corr.}$) and shifts it slightly to the negative direction.

Adsorption isotherm

The adsorption of the organic compounds can be described by two main types of interaction: physical adsorption and chemisorption, that are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. If one supposes that the adsorption of this inhibitor follows the Temkin adsorption isotherm, the degree of surface coverage (θ) was calculated from the results of corrosion weight loss. Here, θ can be given as:

$$\theta = (W_o - W) / W_o \qquad (3)$$

where W_o and W are the corrosion weight losses in absence and in presence of inhibitors.

The degree of surface coverage (θ) for different concentrations of the inhibition in acidic media have been evaluated from electrochemical measurements using the equation:

$$\theta = \frac{i_{free} - i_{inh.}}{i_{free}} \qquad (4)$$

where i_{free} and $i_{inh.}$ are corrosion current densities in absence and in presence of inhibitors.

The degree of surface coverage increases with increase of concentration of the additives, and hence, the inhibition efficiency increases with increasing the concentration of the additives (Figs.2 &3)

Effect of temperature

The effect of temperature on the rate of dissolution of copper in 2 mol dm^{-3} HNO_3 was studied by weight loss method in the range 20-45°C. Arrhenius plot of log k (rate constant) vs.1/T is shown graphically in Fig. 4. The values of activation energy, E*, are given in Table 4. These values indicate that the presence of inhibitors increase the activation energy of the metal dissolution reaction. The inhibitors thus hinder the dissolution reaction and act as corrosion retardant. Also, the results of Table 4 indicate that the presence of the inhibitors increase the free energy (ΔG^*) and enthalpy of activation (ΔH^*) as the inhibition efficiency increases from VII to I. The displacement of water molecules from the metal surface by the organic inhibitor molecules increases the randomness of the system and consequently increases the entropy of activation (ΔS^*). The values of ΔS^* decrease with decreasing inhibition efficiency of the additives as the ability of the inhibitor to displace the water molecules from the metal surface and adsorb instead decreases.

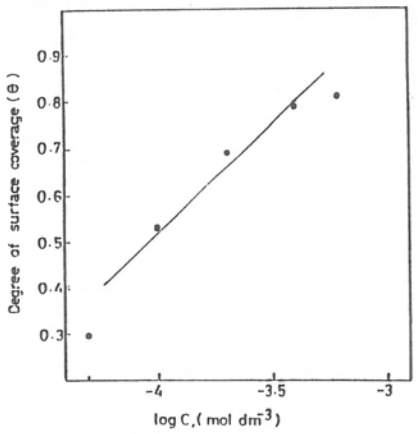


Fig.2. Plot of θ vs. log C for compound II (From weight loss measurements).

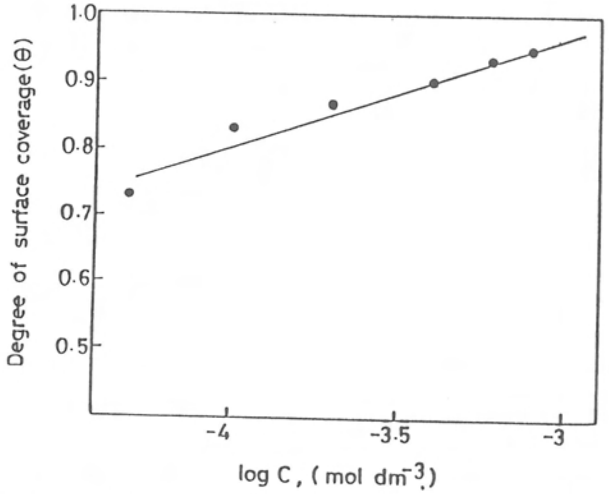


Fig.3. Plot of θ vs. log C for compound II (From polarization measurements).

Table (4):Thermodynamic activation parameters for the corrosion of copper in 2 mol dm^{-3} HNO_3 containing $2x10^{-4}$mol dm^{-3} inhibitors at 25°C.

Inhibitor	ΔH^*(KJ mol.$^{-1}$)	ΔG^*(KJ mol $^{-1}$)	$-\Delta S^*$(J K^{-1})
I	37.84	30.53	24.5
II	45.21	32.18	43.7
III	43.50	31.65	39.7
IV	36.66	3.20	21.7
V	42.36	31.34	37.0
VI	39.45	31.18	27.8
VII	34.38	29.77	15.5

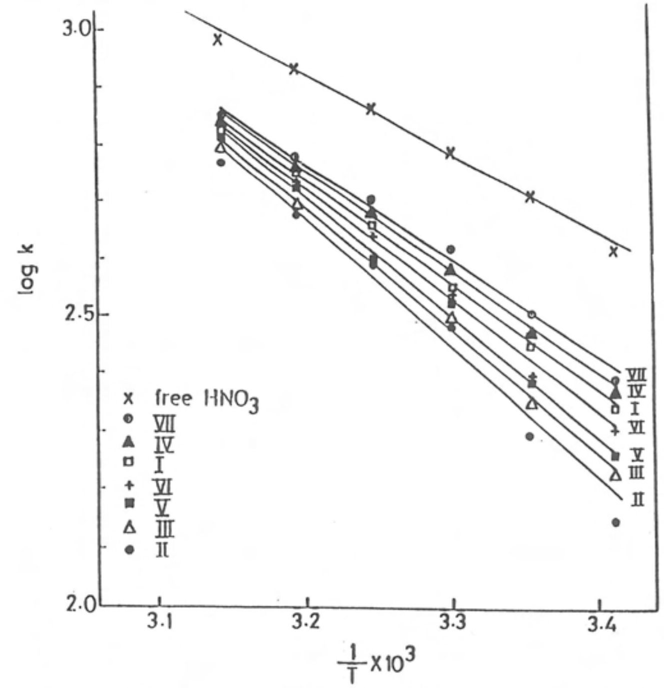


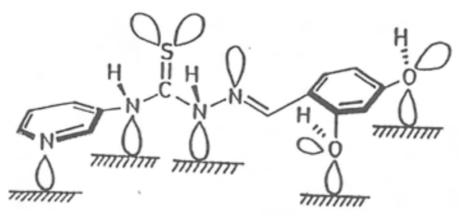
Fig. 4. log k vs. 1/T curves for copper in 2 mol dm^{-3} HNO_3 in absence and presence of $2.0x10^{-4}$mol dm^{-3} of different inhibitors.

Chemical structure and corrosion inhibition

Inhibition of copper in acid solution by the investigated compounds as indicated by weight loss and polarization was found to depend on the concentration and nature of the inhibitors. The observed corrosion data in the presence of inhibitors namely a) the decrease of corrosion rate with increase in concentration of the inhibitor, b) the shift in Tafel lines to higher potential regions and c) the linear variation of weight loss with time indicate that the corrosion inhibition takes place by adsorption of inhibitors at the electrode/solution interface. Thiourea and thiosemicarbazide and their derivatives are known as adsorption type acid corrosion inhibitors. Their adsorption take place through primary and secondly amine nitrogenous and thioketo sulphur. Also, some substituents on the phenyl and pyridine ring may participate in adsorption.

It is known(25) that in an aerated solution, cathodic reaction (oxygen reduction) controls the corrosion of copper. As the cathodic reaction controls the corrosion of copper the inhibitor molecules may preferably be adsorbed in the protonated form. This may account for the superiority of compound II that contains a protonated amino group.

Skeletal representation of the mode of adsorption of the studied thiourea and thiosemicarbazide derivatives (I-VII) is shown in Fig. 5 and clearly indicates the active adsorption sites.



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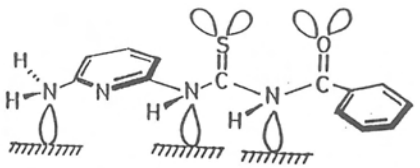

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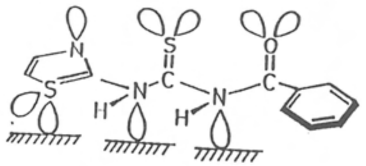

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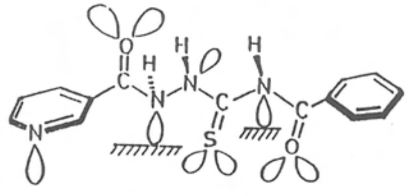

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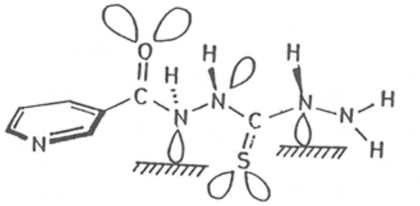

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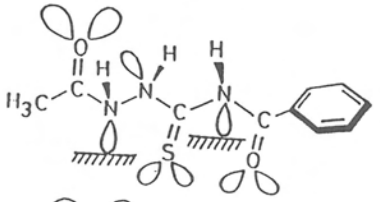

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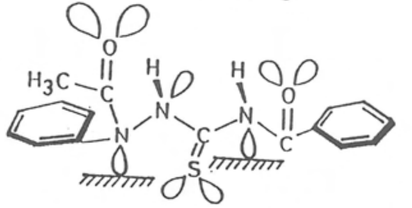

VII

Conclusion

The results of the investigation of inhibitory efficiency of various thiourea derivatives on copper corrosion in 2 mol dm^{-3} nitric acid show that the smallest inhibiting efficiency has compound VII. The inhibition efficiencies increased with increasing concentration of the inhibitor, immersion time and by decreasing temperature. The effectiveness of a corrosion inhibitor depends on the structure of the organic compound. The variation in inhibitive efficiency mainly depends on the type and the nature of the substituents present in the inhibitor molecules

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