"THE USE OF SOME 4-PHENYLTHIOSEMICARBAZONE DERIVATIVES AS CORROSION INHIBITORS FOR COPPER IN NITRIC ACID SOLUTION"

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ABSTRACT

Corrosion inhibition by some 4-phenylthiosemicarbazone derivatives with respect to the dissolution of copper in 2M HNO_3 was measured using electrochemical techniques. Polarization curves indicated that these compounds act as mixed-type inhibitors, i.e. both the cathodic and anodic curves are affected. The observed effect follows the Temkin adsorption isotherm. The effect of the different structural features of these compounds on their inhibition efficiency has been studied. Results indicate that the rate of corrosion of copper increases with increasing temperature over the range 30-60°C both in the absence and in the presence of inhibitors. Some thermodynamic functions were also computed and are discussed.

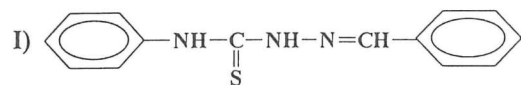**Key words:** Corrosion, copper, nitric acid, 4-phenylthiosemicarbazone derivatives.

INTRODUCTION

The use of nitrogen and sulphur - containing organic compounds as corrosion inhibitors is wide spread for many metals and alloys, little is known of their function because of the complexity of the process. Several mechanisms have been proposed to explain the function of corrosion inhibitors of which the adsorption theory is the most pertinent [1]. The reaction of corrosion inhibitors at the metal-solution interface has been evaluated by adsorption characteristics and also by the thermodynamics of adsorption [2-4].

Copper is widely used in various industrial operations and the study of corrosion of copper and its inhibition is a subject of practical significance. Caffeine and strychnine [5,6], n-decylamine [7], 2,4-dinitrophenylhydraizne [8], benzotriazole [9], benzimidazole [10], 1:2:4 triazole [11] and arylmethylene cyanothioacetamide derivatives [12] have been used as effective acid corrosion inhibitors. Most studies have been concerned with polycrystalline copper surfaces.

The present paper deals with the effect of some 4-phenylthiosemicarbazone derivatives on the corrosion of copper in nitric acid.
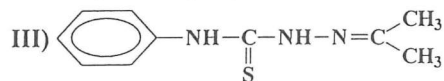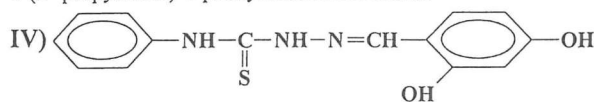
The inhibitors used were:

I) [structure] —NH—C—NH—N=CH— [ring]
     ‖
     S

1-benzylidene-4-phenylthiosemicarbazone

II) [ring] —NH—C—NH—N=CH—CH=CH— [ring]
      ‖
      S
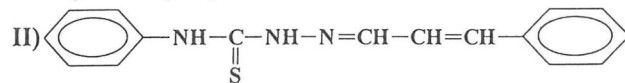
1-cinnamylidene-4-phenylthiosemicarbazone

III) [ring] —NH—C—NH—N=C<CH₃/CH₃
       ‖
       S

1-(2`-propylidene)-4-phenylthiosemicarbazone

IV) [ring] —NH—C—NH—N=CH— [ring] —OH
      ‖ |
      S   OH

1-(2`,4`-dihydroxybenzylidene)-4-phenylthiosemicarbazone

EXPERIMENTAL

Copper test samples containing 0.001% Fe, 0.01% Cd, 0.1% Pb and Cu remainder were used, all chemical were a.r. quality. The solution of 2M HNO_3 was prepared with twice-distilled water.

Polarization experiments were carried out under unstirred conditions with a fine Luggin capillary to avoid ohmic polarization. Galvanostatic condition was maintained using a constant current (WP-704 AX). Copper was taken in the form of cylindrical rod with a surface area of 0.2 cm². The surfaces to be exposed were successively mechanically polished with 500 emery paper using an alcohol as lubricant, degreased in 1:1 HNO_3 and washed thoroughly with distilled water. a saturated calomel electrode and platinum electrode were used as reference and auxiliary electrodes, respectively. For each experiment a new specimen was used. The potentials were recorded using Orion digital ionalyzer (model 701 A). All experiments were carried out according to Gatos [13], and in thermostat at temperature 25±0.2°C. The inhibitive efficiency was calculated from the formula

$$\%Inhibition = \left(1 - \frac{i_i}{i_o}\right) \times 100 \qquad (1)$$

where i_i and i_o are the corrosion currents with and without inhibitor, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the anodic and cathodic Tafel plots of copper in the presence of different concentrations of compound II. For comparison, polarization curves measured in blank solution are also plotted. These compounds induce an increase in both cathodic and anodic overvoltages and cause a parallel displacement of both the cathodic and the anodic Tafel curves. The results indicate that the presence of these compounds in solution inhibits both the cathodic and anodic reactions. The data suggest that these compounds act as mixed-type inhibitors. The corrosion current density, $i_{corr.}$, for copper in 2M nitric acid is 25 μA cm^{-2}. Addition of the compounds tested induce a decrease in $i_{corr.}$, this indicates that these compounds act as inhibitors for copper dissolution in nitric acid.
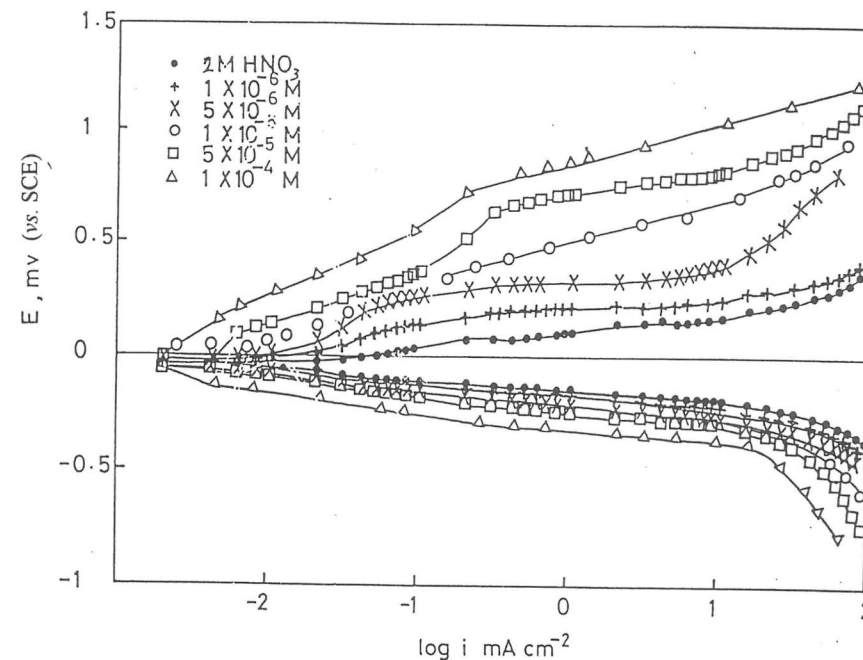

Fig. 1. Galvanostatic polarization curves of copper in 1M HNO_3 solution contianing various concentrations of compound II.

Table 1 gives the effect of concentration of compound II on $i_{corr.}$, anodic and cathodic Tafel slopes (β_a and β_c), $E_{corr.}$, and percentage inhibition efficiency. It can be seen from Table 1 that, as the concentration increases, the value of $i_{corr.}$ decreases and hence the percentage inhibition increases. This indicates that the inhibition efficiency depends on the concentration of the inhibitors. Similar behaviour was observed in the presence of different inhibitors. The data show that the

slopes of the cathodic and anodic Tafel lines (β_c and β_a) remain almost unchanged on increasing the concentration of the tested compounds and have the values $\beta_c = 119\text{-}125$ and $\beta_a = 113\text{-}127$ mv/decade. This behaviour indicates that the adsorbed compounds mechanically screen the coated part of the electrode and therefore protect it from the action of the corrosive medium. This becomes evident from the fact that when θ (θ = fraction of the surface covered by the inhibitor = $1 - i_{inh}/i_{free}$) is plotted against log (inhibitor concentration) straight lines are obtained, indicating that the adsorption of the inhibitor molecules follows the Temkin adsorption isotherm.

Table 1. Corrosion current densities, Tafel slopes and percentage of inhibition efficiency for copper in 2M HNO$_3$ solution in the absence and in the presence of different concentrations of compound II.

Conc. M	$E_{corr.}$ mV	$i_{corr.}$ $\mu A/cm^2$	β_a	β_c	%Inhibition
			mv/decade		
0.0	25	25	127	123	-
1×10^{-6}	30	8.0	115	123	68.0
5×10^{-6}	40	6.2	115	120	75.0
1×10^{-5}	42	5.0	113	120	80.0
5×10^{-5}	44	3.0	113	120	88.0
1×10^{-4}	45	2.0	113	120	92.0

The experimental results (Fig. 2) are in good agreement with the following equations 2 and 3 showing that the adsorption of the additives used follow the Temkin adsorption isotherm

$$\theta = \text{const.} + (2.303/f).\log C \tag{2}$$

$$f = \left(\frac{1}{RT}\right).\frac{d\Delta G^*}{d\theta} \tag{3}$$

It is evident from Table 2 at 1×10^{-5}M different inhibitors that the order of increasing inhibition efficiency of the tested compounds in 2M nitric acid is IV > II > I > III.

Table 2. Corrosion current densities ($i_{corr.}$), Tafel slopes (β_a & β_c) and inhibition efficiency (%I) in 2M HNO$_3$ + 1×10^{-5}M inhibitors for copper at 303 K.

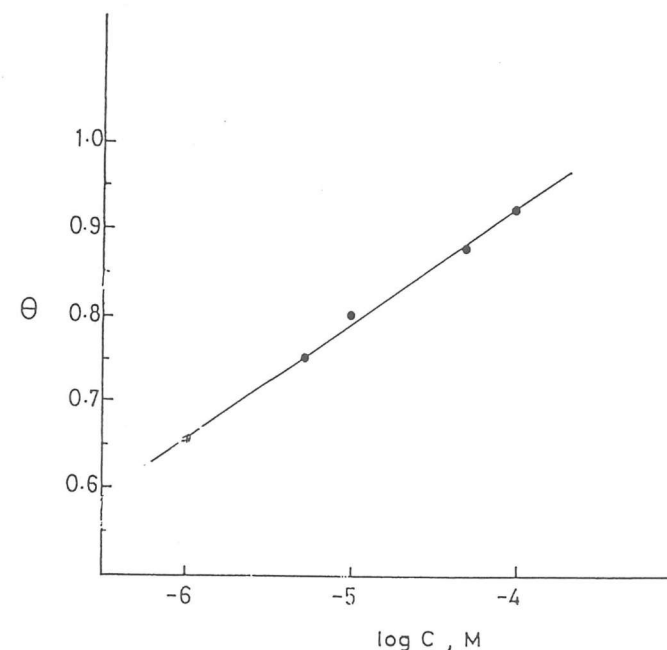| Inhibitor	$E_{corr.}$ mV	$i_{corr.}$ $\mu A/cm^2$	β_a	β_c	%I
			mv/decade		
0.0	25	25.0	127	123	-
I	42	6.2	115	119	75.2
II	42	5.0	113	120	80.0
III	43	9.5	114	121	62.0
IV	45	2.5	115	125	90.0

Fig.2 : Variation of the surface coverage (θ) with the logarithm of compound II concentration

The inhibition efficiency of additives depends on many factors which include the number of adsorption sites and their charge density, molecular size and mode of interaction with the metal surface. Retardation of copper dissolution by the additives is expected to be due to their adsorption on the metal surface via nitrogen atoms numbers 1 and 2 as in the skeletal representation (Fig. 3) of the mode of adsorption of the tested compounds.

Compound IV is found to be the most efficient inhibitor. This is may be due to the presence of four centers of adsorption (two nitrogen atoms 1 & 2 and two oxygen atoms from the hydroxyl groups). The other three inhibitors III, II and I have only two centers of adsorption (two nitrogen atoms 1 & 2), but compound II has higher molecular size so, it comes after compound IV in inhibition efficiency. Compound I comes after compound II. This may due to its lower molecular size than compound II, so lower surface coverage and hence lower inhibition efficiency. Compound III is the least one in inhibition efficiency. This is because it has the lowest molecular size and also the branching in the molecule lowers the inhibition efficiency.
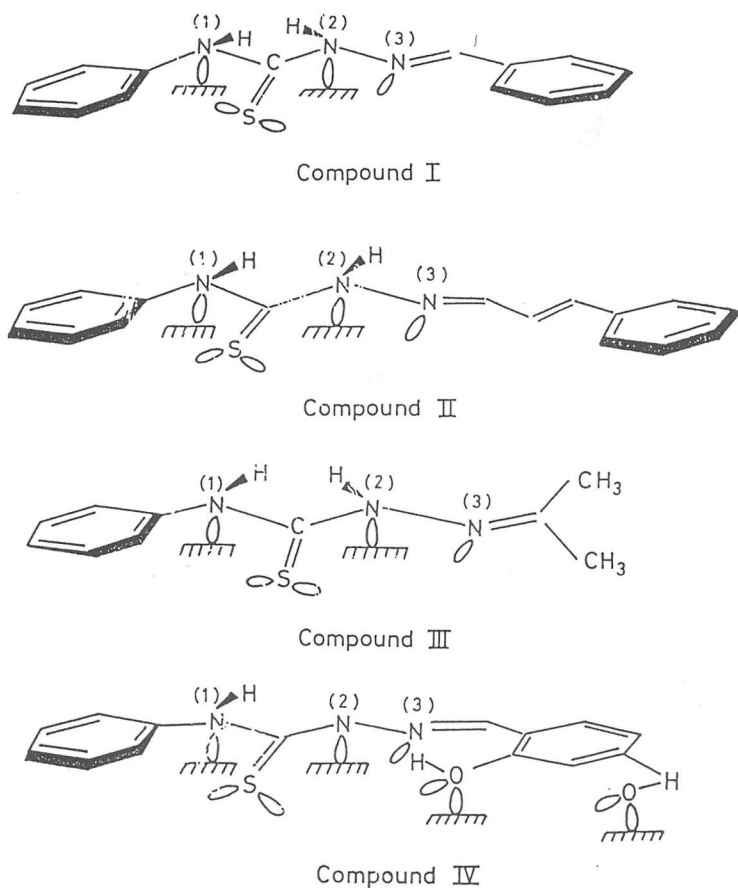
Compound I

Compound II

Compound III

Compound IV

Fig. 3 : Skeletal representation of the mode of adsorption of the tested compounds.

The effect of temperature on the dissolution of copper in the presence and in the absence of additives has been studied by the polarization technique. The corrosion rates were also determined at 30°C, 35°C, 40°C and 45°C in the presence of 1×10^{-5} M inhibitors. From the previous experimental findings it is evident that the corrosion rate increases with increasing temperature, a result which is in accordance with the Arrhenius law in the temperature range used (Fig. 4). The plots are rectilinear and the activation energies are calculated from the slopes of the curves. The Arrhenius activation energy values, obtained from the slopes of log i_{corr}. vs. 1/T are presented in Table 3. These values increase with increasing inhibition efficiency of the additives and suggest that the process is controlled by the surface reaction, since the energy of activation for the corrosion process is in the range of 5 Kcal [14].

The values of free energy of adsorption for each concentration of inhibitors are calculated. The entropy of adsorption is also evaluated. From the values of ΔG^* and ΔS^*, the heat of adsorption (ΔH^*) is calculated (Table 3). The negative values of ΔG^* and the positive values of ΔS^* indicate the spontaneous adsorption of inhibitors on copper. One could thus expect the degree of adsorption by these inhibitors on copper to be in the order: IV > II > I > III. This is also in agreement with the observed corrosion data.
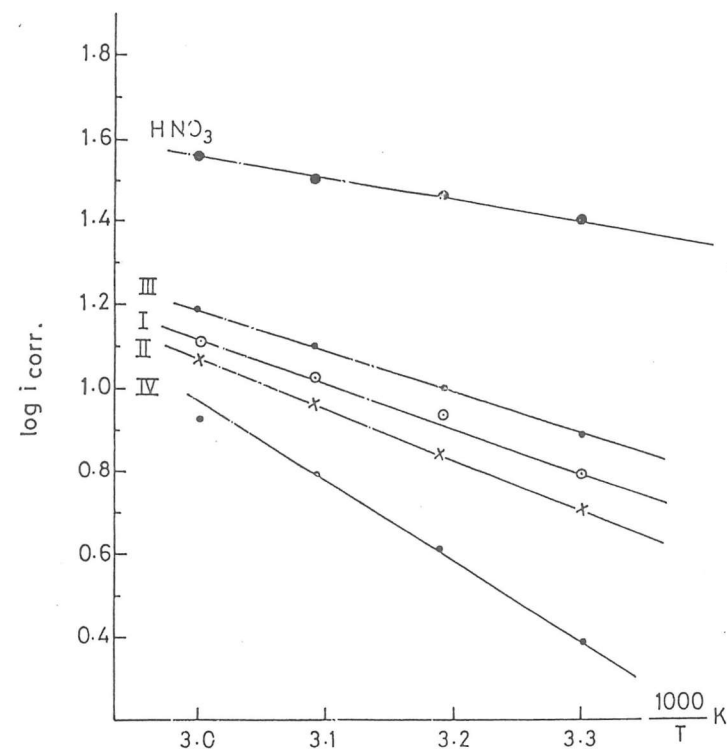

Fig. 4: Arrhenius plot of log i_{corr}. against 1/T in 1M HNO_3 solution in presence and absence of 1×10^{-5} M inhibitors.

Table 3. Energy E*, enthalpy change (ΔH*), entropy change (ΔS*) and free energy of activation change (ΔG*) for copper dissolution in 2M HNO$_3$ in presence of 1x10^{-5}M of different inhibitors at different temperatures (E*, ΔH* and ΔG* Kcal mol^{-1}, ΔS* = cal mol^{-1} K^{-1}).

Temp., K	303	313	323	333
I				
E*		4.14		
ΔH*	4.75	4.77	4.79	4.81
-ΔS*	39.31	39.17	39.10	39.09
ΔG*	16.66	17.03	17.42	17.83
II				
E*		5.06		
ΔH*	5.67	5.69	5.71	5.73
-ΔS*	37.03	36.93	37.03	37.06
ΔG*	16.89	17.25	17.67	18.07
III				
E*		3.68		
ΔH*	4.29	4.31	4.33	4.35
ΔS*	40.30	40.61	40.62	40.60
ΔG*	16.50	17.02	17.45	17.87
IV				
E*		5.68		
ΔH*	6.59	6.61	6.63	6.65
ΔS*	35.84	35.08	34.89	34.89
ΔG*	17.45	17.59	17.90	18.27
2M HNO$_3$				
E*		3.13		
ΔH*	3.74	3.76	3.78	3.80
-ΔS*	40.17	40.35	40.46	40.51
ΔG*	15.91	16.39	16.85	17.29

Conclusions

The tested 4-phenylthiosemicarbazone derivatives act as mixed-type inhibitors in 2M HNO$_3$ at 298 K.

Each compound is adsorbed in accordance with Temkin adsorption isotherm. Inhibitor efficiency increases with increasing molecular size and absence of steric crowding. The corrosion rates decrease with increasing the concentration of the inhibitors and increase with temperature rise.

REFERENCES

1. Hackerman N. and Hurd R.M., 1st Cong. Metallic Corros. London, 1961, p. 166 Butterworths (1962).
2. Rudresh H.B. and Mayanna S.M., J. Electrochem. Soc., 124, 340 (1977).
3. Mayanna S.M., J. Electrochem. Soc., 122, 251 (1975).
4. Dinnappa R.K. and Mayanna S.M., J. Appl. Electrochem. Soc., 11, 111 (1981).
5. Ahmed M.F., Mayanna S.M. and Pushpanaden F., J. Electrochem. Soc., 124, 1667 (1977).
6. Subramanyam N.C., Sheshadri B.S. and Mayanna S.M., Br. Corros. J., 19, 177 (1984).
7. Rudresh H.B. and Mayanna S.M., Br. Corros. J., 12, 54 (1977).
8. Siddagangappa S., Mayanna S.M. and Pushpanaden F., Anti-Corrosion, 23, 11 (1978).
9. Mayanna S.M. and Setty T.H.V., Corros. Sci., 15, 627 (1975).
10. Lewis G., Corros. Sci., 22, 579 (1982).
11. Fox P.G. and Bradley P.A., Corros. Sci., 20, 643 (1980).
12. A.S. Fouda, A.K. Mohamed and H.A. Mostafa, J. Chim. Phys. (Fr), 15, 45 (1998).
13. Gatos H.S., Corrosion, 12, 23 (1956).
14. Fouda A.S., Elaskalny A.H. and Madkur L.H., Ind. J. Chem. Soc., 61, 425 (1984).