INHIBITION OF CORROSION OF COPPER IN NITRIC ACID

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It has been found that aniline, n-butylamine, sodium phosphate and sodium sulphate act as inhibitors in the corrosion of copper in 2.0 N HNO_3. The effect of inhibitor concentration, immersion time and temperature on the corrosion of copper has been also studied. Polarization measurements have been carried out and the Tafel slopes evaluated. Activation energies have been calculated.

Key words: Corrosion inhibitor; Copper corrosion.

INTRODUCTION

Because of the widespread use of copper in industrial applications, the study of its corrosion is of a special interest. Copper has valuable properties such as high electrical and thermal conductivities and resistance to atmospheric corrosion in natural conditions. Hence, the corrosion of copper in various media has been the subject of many investigators [1-6].

The present study is concerned with the effect of aniline, *n*-butylamine, sodium phosphate and sodium sulphate on the corrosion rate of copper in 2.0 N HNO_3 solution using weight loss as the measure and galvanostatic methods.

EXPERIMENTAL

The acid and all inhibitors used were of A.R. grade. All solutions were prepared in double distilled water. Copper sheets (99.98%) of 2 x 2 cm. were used. The specimens were polished successively with a suitable grades of emery paper and then thoroughly cleaned with distilled water and acetone. All experiments were carried out in an air thermostat maintained at $25^\circ \pm 0.1^\circ$. The weight loss during dissolution was determined by estimating the amount of copper dissolved colorimetrically. Inhibitor efficiency was calculated by the equation:

$$E = \frac{Wu - Wi}{Wu} \times 100$$

where E is the percentage inhibition efficiency, Wu is the weight loss in uninhibited solution and Wi is the weight loss in inhibited solution. The potentials were measured vs. calomel reference electrode using a precision potentiometer and a galvanometer.

RESULTS AND DISCUSSION

The corrosion of copper in nitric acid in the absence and presence of aniline, *n*-butylamine, sodium phosphate and sodium sulphate has been investigated using weight loss and galvanostatic methods.

The corrosion rate (mg./sq. dm./hr.) is found to depend on acid concentration. Fig. 1 shows that the corrosion rate increases linearly with nitric acid concentration.

It has been observed that all studied compounds decrease the corrosion of copper in 2.0 N HNO_3 at all concentration used. The data given in Table 1 show that as the concentration of organic and inorganic inhibitors increases, the corrosion rate (mg./sq. dm./hr.) decreases. The two inorganic inhibitors possess high inhibitor efficiency. But in the case of organic inhibitors aniline possesses a high inhibitor efficiency while *n*-butylamine exhibits relatively low inhibitor efficiency.

The high inhibitor efficiency observed in the presence of soidum phosphate may be due to the formation of a semiglassy phosphate layer [7] protecting the metal surface to some extent. On the other hand the high inhibitor efficiency noticed in the presence of sodium sulphate may be due to the formation of adsorbed sulpahte layer on metal surface which prevents to some extent its dissolution. The copper surface in acid solution is positively charged, which in turn enhances the adsorption of anions on the surface [8].

The low inhibitor efficiency in the presence of *n*-butylamine with respect to aniline may be due to the aromatic nature of aniline. Accordingly, the adsorption of
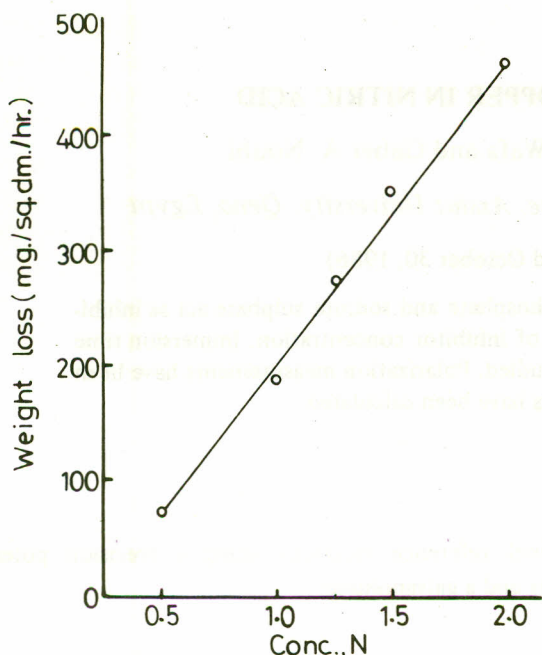
Fig. 1. Effect of HNO_3 concentration on the corrosion rate of Cu.

Table 1. Effect of inhibitor concentration on the corrosion rate of copper (mg./sq. dm./hr.) in 2.0 N HNO_3 at 25° (values in brackets show % inhibition)

Conc. of inhibitor (mM)	Aniline	n-Buty-lamine	Na₃PO₄	Na₂SO₄
0.0	464	464	464	464
5.0	394	457	349	385
	(15.0)	(1.5)	(24.7)	(17.0)
10.0	307	429	288	320
	(33.8)	(7.5)	(38.0)	(31.0)
15.0	222	400	199	250
	(52.1)	(13.8)	(57.1)	(46.1)
20.0	185	366	125	194
	(60.1)	(21.1)	(73.0)	(58.1)
30.0	144	325	93	167
	(68.9)	(30.0)	(80.0)	(64.0)
50.0	116	269	61	137
	(75.0)	(42.0)	(86.8)	(70.4)

aniline on copper surface may be easier than that of *n*-butylamine.

Anodic and cathodic polarization studies have been carried out in 2.0 N HNO_3 in the absence and presence of inhibitors (50 mM). Fig. 2 shows a plot of potential vs. logarithm of the polarization current density. From this figure it is obvious that in all cases the cathode is more polarized than anode. Furthermore, cathodic polarization increased significantly with the addition of inhibitors while anodic polarization is unaffected. And it has been observed that all the anodic Tafel plots lie nearly on the same line, with a constant slope of about 35 mV/decade (± 1) in 2.0 N HNO_3 in the absence and presence of inhibitors (50 mM). The Tafel slope (180 mV/decade) in 2.0 N HNO_3 obtained from cathodic Tafel plot is altered to 285 mV, 290 mV, 300 mV and 335 mV/decade in the presence of 50 mM of *n*-butylamine, Na_2SO_4, aniline and Na_3PO_4 respectively. These observations reveal that the studied organic and inorganic inhibitors interfere with the cathodic reaction without affecting the anodic reaction.

Copper was immersed in 2.0 N HNO_3 in the absence and presence of inhibitors (50 mM) for different periods of time. The results obtained have been recorded in Table 2.

From this Table it is clear that the weight loss (mg./sq. dm.) increases vigorously with time. But in the presence of inhibitors it is interesting to note that (with the exception of aniline) the inhibitor efficiency slightly decreases with time up to about 3 hr and starts to increase again. The decrease in the inhibitor efficiency in the presence of *n*-butylamine, Na_2SO_4 and Na_3PO_4 may be attributed to HNO_2 formed during the dissolution of copper in nitric acid. Hence the corrosion is increased as a result of the autocatalytic effect of HNO_2 and consequently the inhibitor efficiency is decreased. The increased in the inhibitor efficiency (after about 3 hr) may be ascribed to the passiva-
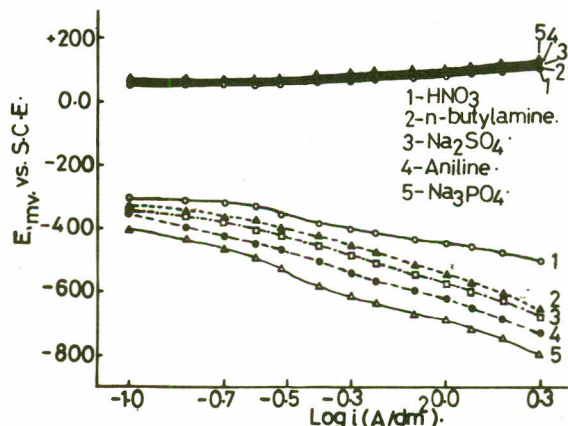

Fig. 2. Anodic and cathodic polarization of Cu in 2.0 N HNO_3 in the absence and presence of inhibitors (50 mM).

Table 2. Effect of time on weight loss of copper (mg./ sq. dm.) in 2.0 N HNO$_3$ in absence and presence of 50 mM of inhibitors (values in the brackets show % inhibition).

Inhibitor	Time (hr.)					
	½	1	2	3	4	5
Nil	108	464	1040	2106	3893	4752
	28	116	247	488	876	1031
Aniline						
	(74.0)	(75.0)	(76.2)	(76.8)	(77.5)	(78.3)
	64	269	645	1327	2414	2723
n-Butylamine						
	(40.7)	(42.0)	(37.9)	(37.0)	(38.0)	(42.7)
	13	61	204	463	915	975
Na$_3$PO$_4$						
	(87.9)	(86.8)	(80.4)	(78.0)	(76.5)	(79.5)
	30	137	364	779	1472	1630
Na$_2$SO$_4$						
	(72.2)	(70.4)	(65.0)	(63.0)	(62.2)	(65.7)

Table 3. Effect of temperatue on corrosion rate of copper (mg./sq. dm./hr.) in 2.0 N HNO$_3$ in absence and presence of 50 mM of inhibitors (values in brackets show % inhibition)

Inhibitor	Temperature °C			
	25	30	40	50
Nil	464	1308	5636	13216
	116	301	1262	2841
Aniline				
	(75.0)	(77.0)	(77.6)	(78.5)
	269	756	3212	7269
n-Butylamine				
	(42.0)	(42.2)	(43.0)	(45.0)
	61	144	564	1163
Na$_3$PO$_4$				
	(86.8)	(89.0)	(90.0)	(91.2)
	137	353	1494	3304
Na$_2$SO$_4$				
	(70.4)	(73.0)	(73.5)	(75.0)

tion of the surface and the consumption of acid in the corrosion process.

The inhibitor efficiency in the presence of aniline slightly increases with immersion time. This behaviour may

be due to the reaction of aniline with HNO$_2$ formed to form a diazonium compound and therefore prevent or decrease its catalytic action on the corrosion process [9, 10].

Fig. 3 shows the variation of corrosion potential in 2.0 N HNO$_3$ with time both in the absence and presence of 50 mM of inhibitor. From Fig. 3 it is obvious that the potential shifted to the noble direction with immersion time both in HNO$_3$ alone and in presence of inhibitors, while the corrosion potential in the presence of inhibitor shifted to more negative direction than that in nitric acid alone. The extent of shift is dependent on the nature of the inhibitor. In other words the corrosion potential in the presence of inhibitors is more negative than that in nitric acid alone.
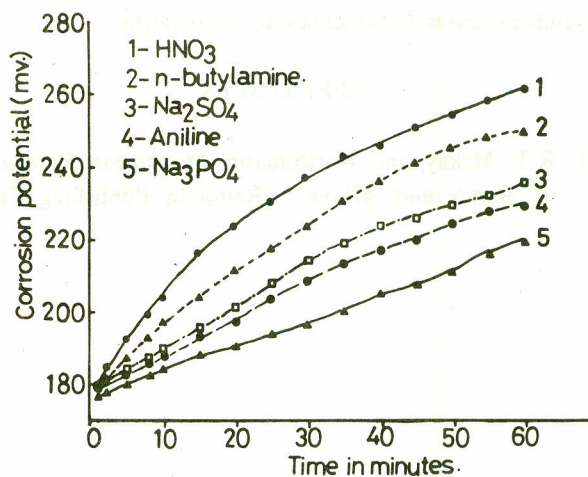

Fig. 3. Variation of corrosion potential with time in 2.0 N HNO$_3$ and 2.0 N HNO$_3$ containing 50 mM inhibitor.
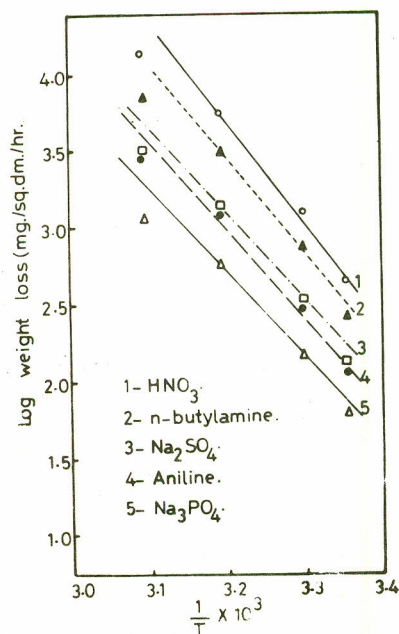

Fig. 4. Log weight loss $\frac{1}{T}$ plot.

The effect of temperatue on the corrosion rate (mg./sq. dm./hr.) of copper in 2.0 N HNO_3 in the absence and presence of inhibitors (50 mM) has been investigated (Table 3). From Table 3 it is clear that the corrosion rate increases with rising temperatue of the corroding medium (without and with inhibitors). While it is observed the inhibitor efficiency is improved with rising temperature to some extent, activation energies for the corrosion of copper in 2.0 N HNO_3 in the absence and presence of inhibitors are calculated from Arrhenius plots (Fig. 4). The values of activation energy are 30.93, 26.12, 27.49, 25.2 and 25.2 K. Cal./mole in 2.0 N HNO_3 alone and in the presence of n-butylamine, aniline, sodium sulphate and sodium phosphate respectively. Thus the protectivity of these compounds increases with increase in temperature.

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