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STUDY OF INHIBITIVE EFFECTS OF SOME SCHIFF BASES ON COPPER METAL IN ACIDIC MEDIA BY MASS LOSS TECHNIQUES

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ABSTRACT

A new class of corrosion inhibitors namely Schiff base were synthesized and its inhibiting action on the corrosion of copper metal in HCl was investigated by various corrosion monitoring techniques. Mass loss techniques have been employed to study of the corrosion inhibition of some newly synthesized Schiff bases viz. N-(2- Methoxy bezalidine)-2- Amino pyrimidine(SB_1), N- (3-Methoxy benzalidine)-2-Amino pyrazine (SB_2) for copper metal in HCl solutions. The inhibition was assumed to occur via adsorption of the inhibitor molecule on the metal surface. Results of inhibition efficiencies from the mass loss technique shows that Schiff bases are good inhibitors in acidic solution. Inhibition efficiency increases with the increase in the concentration of acid as well as those of inhibitors. Maximum inhibition efficiency is shown at highest concentration of Schiff bases in acidic medium.

Key words: Schiff bases, Corrosion, Inhibition efficiency, Corrosion rate, Surface coverage.

INTRODUCTION

One of the most vital processes in the field of prevention of corrosion and its control is the use of organic inhibitors. The crucial part in the mechanistic aspect of such inhibitors is the specific interaction between certain functionalities in the inhibitors with the corrosion active centre on the metal surface. Copper is an important metal regarding to its wide applications in industry in various mechanical and structural purposes. It is much prone to corrosion while in use by different corrosion agents of which acids like HCl and H_2SO_4 are most common and dangerous. HCl and H_2SO_4 have been used for drilling operations, picking baths and in decaling processes[1].

Corrosion of copper and its alloys in different acid media has been extensively studied[2-5]. Corrosion rate of copper is affected by pH of solution, metal dissolved oxygen

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and temperature. It is adversely affected in the pH range 4 to 10 but fairly resistant to attack by alkali. The effects of certain organic compounds bearing hetero atoms have been studied as corrosion inhibitors for copper. Many investigators have studied the effect of some nitrogen containing compounds on corrosion of copper in different acid media. Extracts of some naturally occurring Plants containing some alkaloids have also been found effective corrosion inhibitors in hydrochloric acid for copper.

Generally the heterogeneous organic compounds having higher basicity and electron density on the hetero atoms like O, N, S have tendency to resist corrosion. Heteroatom such as N, O, S present in the inhibitors plays in the leading role in this interaction by donating their free electron pair. Hence most of the organic compounds containing these heteroatom act as good inhibitors. In addition, compounds with multiple bond behave as efficient inhibitors due to the availability of π (pi) electron in the same molecules for interaction with metal surface. Nitrogen and sulphur are the active centers for the process of adsorption on the metal surface.[6-15]

EXPERIMENTAL

A rectangular specimens of copper of dimension 2.0 cm x 2.0 cm x 0.05 cm containing a small hole of about 2 mm diameter near the upper edge were taken. Specimens were cut from the centre of a sheet and were thoroughly cleaned, buffed, rubbed with emery paper to obtain mirror like spotless surface. The specimens were finally degreased by using acetone or dioxane. All chemicals used for the synthesis of Schiff's bases were of analytical reagent (A.R.) grade and solutions of hydrochloric acid were prepared in double distilled water.

All the Schiff bases were prepared by conventional method i.e. by refluxing equimolar quantities of respective aldehydes and amines. Each specimen was suspended by a V-shaped glass hook made by fine capillary glass tubes and immersed in a glass beaker containing 50 mL of test solutions at room temperature. After the test, specimens were cleaned with running water and dried with hot air drier and then weighed again. The percentage inhibition efficiency (η %) as[16-20] –

$$\eta\ \% = \frac{\Delta M_u - \Delta M_i}{\Delta M_u} \times 100 \qquad \ldots(1)$$

where ΔM_u is the weight loss in uninhibited solution and ΔM_i is the weight loss in inhibited solution. Corrosion rate (C.R.) can be determined from the loss in mass as follows[21-23].

$$\text{C.R. (mm/py)} = \frac{87.6 \text{ X } \Delta M}{A \times D \times T} \qquad \ldots(2)$$

Where ΔM is the loss of mass in mg, A is the exposed area of the metal specimen in cm^2, D is the density in gm/cm^3 and T is time of exposure in hours. Surface coverage (θ) of metal specimen by inhibitor was calculated as[24-30].

$$\text{Surface coverage } (\theta) = \frac{\Delta M_u - \Delta M_i}{\Delta M_u} \qquad \ldots(3)$$

Where ΔM_u is the mass loss in uninhibited acid, ΔM_i is the mass loss in inhibited acid.

RESULTS AND DISCUSSION

Mass loss (ΔM) and percentage inhibition efficiencies (η %) for different concentrations of HCl and inhibitors are shown in Table 1. It is observed that percentage inhibition efficiency (η %) increases with increase in the concentration of the acids and also with the increase in the concentration of inhibitors.

A comparative study of inhibitive effects of some Schiff bases :

Table 1: Mass loss and inhibition efficiency (η %) for copper metal in HCl solution with given inhibitor additions; Temperature:- 30 ± 0.1°C

Inhibitor Conc. %	0.1 N HCl	72 h	0.5 N HCl	48 h	1 N HCl	24 h	2N HCl	4 h
	ΔM, mg	η %	ΔM, mg	η %	ΔM, mg	η %	ΔM, mg	η %
Uninhibited	21.3	-	30.5	-	42.5	-	47.5	-
SB_1								
0.5	13.4	37.08	13.3	56.39	13.1	69.17	13.9	70.73
1.0	12.4	41.78	12.9	57.48	12.3	71.05	11.9	74.94
2.0	10.6	50.23	10.0	66.91	11.7	72.47	10.3	78.31
5.0	8.9	58.21	9.2	69.67	10.2	76.00	9.8	79.36
SB_2								
0.5	13.7	35.68	14.2	53.44	16.2	61.88	16.4	65.47
1.0	12.9	39.43	12.6	58.68	13.9	67.29	14.5	69.47
2.0	11.6	45.53	12.1	60.32	13.4	68.47	13.9	70.73
5.0	10.9	48.82	11.5	62.29	12.9	69.64	12.8	73.05

The two new Schiff bases show maximum inhibition efficiency at the highest concentration of the acid 2N at their highest concentration i.e. 5.0 %.

Corresponding corrosion rate and surface coverage (θ) for HCl solutions are depicted in Table 2. It is observed from table that corrosion rate of copper metal decreases with the increase in the concentration of inhibitors whereas corrosion rate increases with the increase in the strength of HCl solutions.

Table 2: Corrosion rate (mm/yr) and surface coverage (θ) for copper metal in HCl solution with given inhibitor additions; Temperature- 30 ± 0.1°C. Effective area of specimen: 4 cm^2

Inhibitor conc. %	**0.1 N HCl 72 hrs.**		**0.5 N HCl 48 hrs**		**1 N HCl 24 hrs.**		**2 N HCl 4 hrs**	
	C. R. mm/yr	**Surface coverage (θ)**	**C.R. mm/yr**	**Surface coverage (θ)**	**C.R mm/yr.**	**Surface coverage (θ)**	**C.R. mm/yr**	**Surface coverage (θ)**
Uninhibited	0.45	-	0.82	-	9.50	-	10.40	-
SB$_1$								
0.5	0.20	0.37	0.35	0.56	3.50	0.69	4.40	0.70
1.0	0.18	0.41	0.23	0.57	2.70	0.70	3.10	0.74
2.0	0.13	0.50	0.19	0.66	2.10	0.72	2.90	0.78
5.0	0.08	0.58	0.13	0.69	1.30	0.76	1.80	0.79
SB$_2$								
0.5	0.27	0.35	0.40	0.53	3.90	0.61	5.12	0.65
1.0	0.19	0.39	0.27	0.58	2.98	0.67	4.14	0.69
2.0	0.17	0.45	0.21	0.60	2.42	0.68	3.15	0.70
5.0	0.10	0.48	0.18	0.62	1.62	0.69	2.18	0.73

Surface coverage (θ) of metal specimen by inhibitors increases with the increase in the acid strength as well as with the increase in the concentration of inhibitors. Maximum surface coverage is observed at the highest concentration of acid (2N) at maximum concentration (5.0).

Surface coverage (θ) and log [θ/1- θ] values of copper metal in HCl solutions are depicted in Table 3. It is observed from the table that as surface coverage increases, the value of log [θ/1- θ] also increases.

Table 3: Surface coverage (θ) and log [θ/1- θ] for copper metal in HCl solutions with given inhibitor additions. Effective area of specimen: 4 cm^2

Inhibitor Conc. %	0.1N HCl 72 h		0.5 N HCl 48h		1N HCl 24 h		2N HCl 4 h	
	Surface coverage	log [θ/1-θ]	Surface Coverage	log [θ/1- θ]	Surface Coverage	Log [θ/1- θ]	Surface coverage	Log [θ/1- θ]
Uninhibited								
SB$_1$								
O.5	0.37	-0.23	0.56	0.10	0.69	0.34	0.70	0.36
1.0	0.41	-0.15	0.57	0.12	0.70	0.36	0.74	0.45
2.0	0.50	0	0.66	0.28	0.72	0.41	0.78	0.54
5.0	0.58	0.14	0.69	0.34	0.75	0.47	0.79	0.57
SB$_2$								
0.5	0.35	-0.26	0.53	0.05	0.61	0.19	0.65	0.26
1.0	0.39	-0.19	0.58	0.14	0.67	0.30	0.69	0.34
2.0	0.45	-0.08	0.60	0.17	0.68	0.32	0.70	0.36
5.0	0.48	-0.03	0.62	0.21	0.69	0.34	0.72	0.41

Generally the organic molecules containing heteroatom like oxygen, sulphur and nitrogen cause blockage of active sites on the metallic surface, thus resulting in the decrease in tne corrosion rate. Organic compounds mostly act via adsorption on metal surface and complex formation. That is the basis of adverse effect of higher temperature on the efficiency of organic compounds. Higher inhibitor concentration and longer exposure of copper in inhibitor solution lead to inhibition efficiency increase. Molecular structure of inhibitor is the main factor determining its characteristics. Presence of heteroatom (S, N, O) with free electron pairs, aromatic ring with delocalized pi electron, high molecular weight alkyl chains, substituent groups in general improves inhibition efficiency. The effect of particular electron group is favorable. Group position is also important. It has been observed that inhibition efficiency is higher in higher concentration of acids.

This may be due to the fact that in strong acidic conditions ionization of Schiff bases increases, which favors the adsorption strongly and thus further reduces the exposed area of metal, which results further increase in inhibition efficiency. Self assembled monolayer of inhibitor show high inhibition efficiency with low inhibitor consumption, which is great advantage of that kind of treatment. Langmuir adsorption isotherm plot (graph between log C and log [θ/1- θ]) for copper metal in 0.1 N HCl containing the inhibitors as Schiff bases are shown in Figure 1.

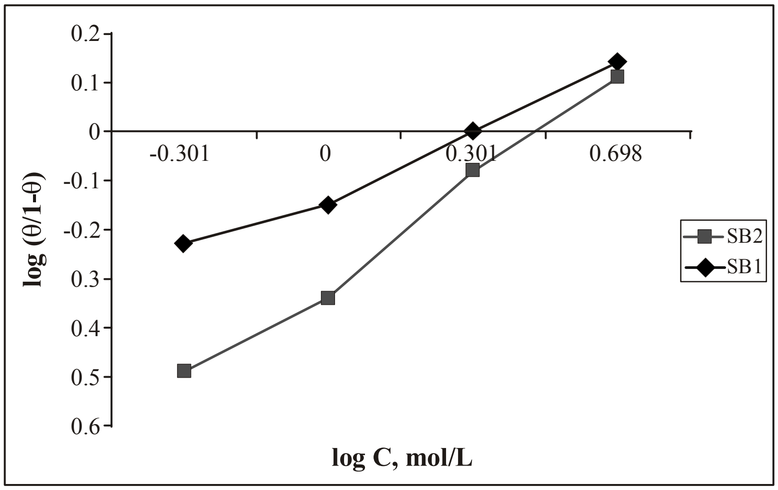

Fig. 1: Langmuir adsorption isotherms for Copper metal in 0.1 N HCl

CONCLUSION

The average weight loss data obtained for the copper specimen for various concentration of inhibitors were presented in Table 1. From the weight loss data, it is clear that the loss in the weight of copper specimen decreases with increasing inhibitor concentration. A study of two synthesized Schiff bases has shown effective corrosion inhibitors for copper metal in HCl acid solutions. Mass loss method has shown that efficiency of inhibitors increase with increasing strength of acid from 0.1 N HCl to 2 N HCl and with increasing concentration of inhibitors in the range from 0.5 % to 2.0 %.

Maximum inhibition efficiency was observed for SB_1. The degree of surface coverage for different concentration of inhibitors has been evaluated from weight loss method. The data were plotted using Langmuir isotherm with log [θ/1- θ] versus log C for all the compounds (Fig. 1). A straight line was obtained in all the case indicating that the adsorption of these compounds on metal surface obeys Langmuir adsorption isotherm. This is due to the fact that molecules of adsorbed species interact with each other on the anodic and cathodic sites on the metallic surface.

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