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STUDY OF SCHIFF BASES AS CORROSION INHIBITORS ON METAL IN ACIDIC MEDIA BY MASS LOSS TECHNIQUES

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ABSTRACT

A new class of corrosion inhibitors namely Schiff base were synthesized. The influence of Schiff base in different concentration of acid on the corrosion behavior of copper in H_2SO_4 was studied by mass loss method. The adsorption of inhibitor on copper metal surface obeys the Langmuir adsorption. Mass loss techniques have been employed to study of the corrosion inhibition of some newly synthesized Schiff bases viz. N-(anisalidine)-2-Amino pyridine (SB_1) N-(Salicylidine)-2-amino-3-methyl pyridine (SB_2) for copper metal in H_2SO_4 solutions. Results of inhibition efficiencies from the mass loss technique shows that inhibition efficiency increased with increase in the concentration of Schiff bases as well as concentration of acid. Maximum inhibition efficiency is shown at highest concentration of Schiff bases in acidic medium.

Key words: Schiff bases, Inhibition efficiency, Corrosion rate, Sulphuric acid.

INTRODUCTION

Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption[1]. Different organic and nonorganic compounds have been studied as inhibitors to protect metals from corrosion attack. Usually, organic compounds that exert a significant influence on the extent of adsorption on the metal surface and therefore can be used as effective corrosion inhibitors. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and p electrons.

Copper and copper based alloys are of considerable importance, as they form the backbone of modern industries. Copper has been widely used for shipboard condensers,

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power plant condensers and petrochemical heat exchangers[2]. It is particularly relevant to the Indian region, where various industries extensively use copper in marine applications and in heat exchanger tubes. Copper materials are relatively noble and for many applications have superior physical and mechanical properties. Corrosion of copper metal in different acid media has been extensively studied[3-7].

In acidic media, the use of sulphuric acid in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble-free compared to other mineral acids[8-10]. Thus, the use of corrosion inhibitors is one of the most practical methods for corrosion protection of steel especially in acidic media[11-14]. Organic compounds containing electronegative functional groups and electrons in triple or conjugated double bonds are usually good corrosion inhibitors. Heteroatoms such as S, P, N and O as well as aromatic rings in their structure are the major adsorption centers. The compounds used as corrosion inhibitors act through a process of surface adsorption[15].

The efficiency of inhibitors depends on the characteristics of the environment in which it acts the nature of the metal surface and electrochemical potential at the interface[16-18]. The structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface also have effect on the efficiency of inhibitors[19-22].

EXPERIMENTAL

Rectangular specimens of copper of dimension 2.0 cm x 2.0 cm x 0.026 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 grade and solutions of hydrochloric acid were prepared in double distilled water.

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[23,24].

$$\eta\ \% = \frac{\Delta M_u - \Delta M_i}{\Delta M_u} \times 100$$

Where ΔM_u is the mass loss in uninhibited solution and ΔM_i is the mass loss in inhibited solution.

Corrosion rate (C.R.) can be determined from the loss in mass as follows.

$$\text{C.R. (mm/py)} = \frac{87.6 \text{ x } \Delta M}{\text{A x D x T}}$$

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[25-26].

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

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 sulphuric acid 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 H_2SO_4 solution with given inhibitor additions; Temperature: - 30 ± 0.1°C

Inhibitor concentration	0.1 N H_2SO_4	72 hrs	0.5 N H_2SO_4	48 hrs	1 N H_2SO_4	24 hrs	2 N H_2SO_4	4 hrs
%	ΔM, mg	η %	ΔM, mg	η %	ΔM, mg	η %	ΔM, mg	η %
Uninhibited	23.5	_	32.5	_	45.3	_	46.5	_
SB_1								
0.5	14.5	38.29	15.5	52.61	14.5	67.99	15.3	67.09
1.0	13.8	41.27	13.6	58.15	12.8	71.74	13.4	71.18
2.0	9.8	58.29	10.3	68.30	12.5	72.40	12.9	72.25

Cont…

Inhibitor concentration	**0.1 N H_2SO_4**	**72 hrs**	**0.5 N H_2SO_4**	**48 hrs**	**1 N H_2SO_4**	**24 hrs**	**2 N H_2SO_4**	**4 hrs**
5.0	8.8	62.55	9.8	69.84	10.9	75.93	11.5	75.26
SB_2								
0.5	9.8	58.29	10.4	68.00	11.3	75.5	12.5	73.11
1.0	8.5	63.82	8.7	73.23	10.4	77.04	10.9	76.75
2.0	7.9	66.38	8.2	74.76	8.5	81.23	8.9	80.86
5.0	7.2	69.36	7.9	75.69	8.1	82.11	8.4	81.93

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 (2 N) at maximum concentration (5.0).

Table 2: Corrosion rate (mm/yr) and surface coverage (θ) for copper metal in H_2SO_4 solution with given inhibitor additions; Temperature- 30 ± 0.1°C. Effective area of specimen: 8 cm^2

Inhibitor conc.	**0.1 N H_2SO_4**		**0.5 N H_2SO_4**		**1 N H_2SO_4**		**2 N H_2SO_4**	
	72 hrs		**48 hrs**		**24 hrs**		**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	0.50	_	0.80	_	7.3	_	9.5	_
SB_1								
0.5	0.28	0.38	0.37	0.52	2.40	0.67	4.90	0.67
1.0	0.21	0.41	0.25	0.58	1.90	0.71	3.20	0.71
2.0	0.17	0.58	0.19	0.68	1.20	0.72	2.50	0.72
5.0	0.15	0.62	0.16	0.69	0.40	0.75	1.90	0.75
SB_2								
0.5	0.30	0.58	0.40	0.68	3.50	0.75	5.70	0.73
1.0	0.23	0.63	0.29	0.73	2.70	0.77	3.90	0.76
2.0	0.19	0.66	0.21	0.74	1.90	0.81	3.10	0.80
5.0	0.16	0.69	0.19	0.75	0.50	0.82	2.10	0.81

Surface coverage (θ) and log [θ/1-θ] values of tin metal in H_2SO_4 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 H_2SO_4 solutions with given inhibitor additions. Effective area of specimen: 8 cm^2

Inhibitor Conc.	0.1 N H_2SO_4 72 hrs		0.5 N H_2SO_4 hrs		1 N H_2SO_4 24 hrs		1 N H_2SO_4 4 hrs	
	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								
0.5	0.38	-0.21	0.52	0.03	0.67	0.30	0.67	0.30
1.0	0.41	-0.15	0.58	0.14	0.71	0.38	0.71	0.38
2.0	0.58	0.14	0.68	0.32	0.72	0.41	0.72	0.41
5.0	0.62	0.21	0.69	0.34	0.75	0.47	0.75	0.47
SB_2								
0.5	0.58	0.14	0.68	0.32	0.75	0.47	0.73	0.43
1.0	0.62	0.19	0.73	0.43	0.77	0.52	0.76	0.50
2.0	0.66	0.28	0.74	0.43	0.77	0.52	0.76	0.50
5.0	0.69	0.34	0.75	0.47	0.82	0.65	0.81	0.62

Generally the organic molecules containing heteroatom like O. S and N cause blockage of active sites on the metallic surface, thus resulting in the decrease in the 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 tin 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 and substituent groups in general improves inhibition efficiency. 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 tin metal in 0.1 N H_2SO_4 containing the inhibitors as Schiff bases are shown in Fig. 1.

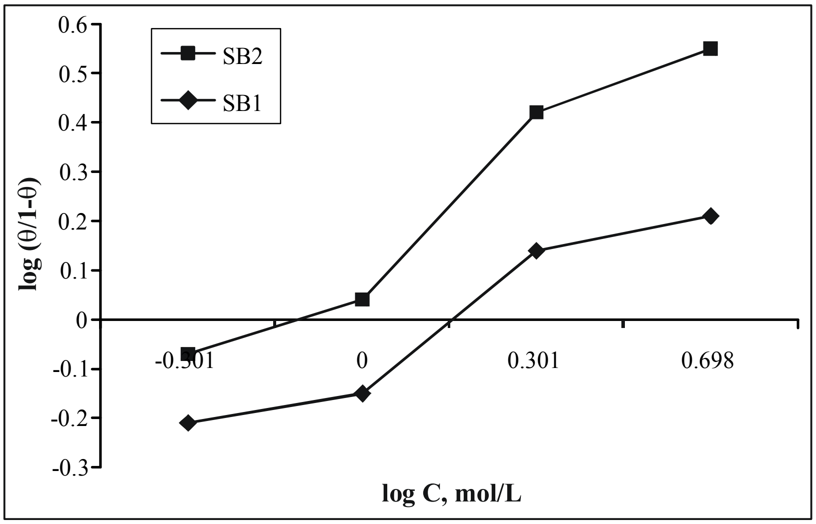

Fig. 1: Langmuir adsorption isotherms for tin metal in 0.1 N H_2SO_4

CONCLUSION

From the mass loss data, it is clear that the loss in the weight of copper specimen decreases with increasing inhibitor concentration. Schiff bases were found to be effective inhibitor for tin corrosion in sulphuric acid solution. The data obtained from weight loss technique for the studied inhibitor fit well into the Langmuir adsorption isotherm. A straight line was observed in all the case indicating that the adsorption of these compounds on metal surface obeys Langmuir adsorption isotherm.

Maximum inhibition efficiency was observed for SB_2. The degree of surface coverage for different concentration of inhibitors has been evaluated from mass loss method. The data were plotted using Langmuir isotherm with log [θ/1-θ] versus log C for all the compounds (Fig. 1).

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