Effect of Schiff's Bases as Corrosion Inhibitors on Mild Steel in Sulphuric Acid

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Abstract: Mass loss and thermometric methods have been used to study the corrosion inhibitory effect of synthesised Schiff's bases *viz.* *N*-(furfurilidine) – 4- methoxy aniline (SB₁), *N*-(furfurilidine) – 4- methylaniline (SB₂), *N*-(salicylidine) – 4- methoxy aniline (SB₃), *N*-(cinnamalidine) – 4 –methoxy aniline (SB₄) and *N*-(cinnamalidine) - 2-methylaniline (SB₅) on mild steel in sulphuric acid solutions. Results show that both methods have good agreement with each other and inhibition efficiency depends upon the concentration of inhibitor as well as that of acid. Maximum inhibition efficiency is shown at highest concentration of Schiff's bases at the highest strength of acid.

Keywords: Schiff's bases, Corrosion, Inhibition efficiency, Corrosion rate, Surface Coverage.

Introduction

Mild steel is an important metal regarding to its wide applications in industry in various mechanical and structural purposes. It is widely used in engineering fabrications like bridge work, buildings, steam engine parts and automobiles etc. It is much prone to corrosion while in use by different corrosion agents of which acids like HCl and H₂SO₄ are most common and dangerous. HCl and H₂SO₄ have been used for drilling operations, picking baths and in decaling processes¹.

Corrosion of mild steel and its alloys in different acid media has been extensively studied²⁻⁵. Corrosion rate of mild steel is affected by pH of solution, metal dissolved oxygen and temperature. It is adversely affected in the pH range 4 to 10 but fairly resistant to attack

by alkali. The effect of certain organic compounds bearing hetero atoms have been studied⁶⁻¹² as corrosion inhibitors for mild steel. Many investigators¹³⁻¹⁵ have studied the effect of some nitrogen containing compounds on corrosion of mild steel in different acid media. Extracts of some naturally occurring Plants containing some alkaloids have also been found effective corrosion inhibitors¹⁶⁻¹⁷ in sulphuric acid for mild steel.

Generally the heterogenous organic compounds having higher basicity and electron density on the hetero atoms like O, N, S have tendency to resist corrosion. Nitrogen and sulphur are the active centers for the process of adsorption on the metal surface.

In the present investigation the inhibition efficiency of five synthesised Schiff's bases viz. *N*-(furfurilidene) – 4- methoxy aniline (SB₁), *N*-(furfurilidene) – 4- methylaniline (SB₂), *N*-(salicylidene) – 4- methoxy aniline (SB₃), *N*-(cinnamalidene) – 4 –methoxy aniline (SB₄) and *N*-(cinnamalidene) - 2-methylaniline (SB₅) have been investigated for mild steel in sulphuric acid.

Experimental

Rectangular specimens of mild steel of approximate composition 99.3% Fe, 0.12% C, 0.4% Mg, 0.14% Si and 0.04% S of dimension 2.5 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 steel sheet and were thoroughly cleaned, buffed, rubbed with emery paper to obtain mirror like spotless surface. The specimens were finally degreased by using acetone. All chemicals used for the synthesis of Schiff's bases were of analytical reagent grade and solutions of sulphuric acid were prepared in double distilled water.

Each specimen was suspended by a V-shaped glass hook made by fine capillary glass tubes and immersed in a glass beaker containing 50mL of test solutions at room temperature. After the exposure of sufficient time the test specimen was taken out, cleaned under running water and finally dried with hot air dryer. The percentage corrosion inhibition efficiency was calculated as¹⁸

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

where, ΔM_u = Mass loss of metal in uninhibited solution.

ΔM_i = Mass loss of metal in inhibited solution.

The degree of surface coverage of metal (θ) was calculated as:

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

The corrosion rate in mmpy (milli mils penetration per year) can be obtained by following equation²⁰.

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \Delta M}{A T d}$$

Where ΔM = Mass loss in mg.

A = Exposed area of metal surface in cm².

T = Time of exposure in hours

d = metal density in gm cm⁻³

and 1 mil = 0.001 inch.

Corrosion inhibition efficiencies were also calculated by other method *i.e.* thermometric method in which the variation of temperature of the system is followed as a

function of time. The method was first introduced by Mylius²¹. The method involves the immersion of single specimen of dimensions 2.5 cm x 2.0 cm x 0.05 cm in an insulating reactions chamber having 50mL of solution at an initial room temperature. Temperature changes were measured at regular intervals using a thermometer with a precision of 0.01°C. The increase in temperature was slow initially and rapid afterwards, reaching a maximum value and then started to decrease. The maximum temperature was noted. Percentage corrosion inhibition efficiencies were calculated as

$$\eta \% = \left(\frac{RN_f - RN_i}{RN_f} \right) \times 100$$

where RN_f = Reaction number in free solution.

RN_i = Reaction number in inhibited solution.

Reaction number $RN (K \min^{-1})$ is defined as :

$$RN = \frac{(T_m - T_i)}{t}$$

where T_m = Maximum temperature attained by solution.

T_i = Initial temperature of solution.

t = Time required to attain maximum temperature.

Results and Discussion

Mass loss and corresponding corrosion inhibition efficiency in different strengths of H_2SO_4 in different concentrations of inhibitors are depicted in Table 1. It is observed from the Table that percentage inhibition efficiency increases with the increase in the concentration of inhibitor. It is also clear from the Table 1 that each inhibitor has higher efficiency at higher concentration of acid and maximum efficiency is shown at the highest concentration of acid (2N). The maximum efficiency (97.01%) was shown by *N*-(salicylidine)-4-methoxy aniline (SB_3).

Inhibition efficiencies were also determined by another method i.e. thermometric method. Since no significant changes in temperature were observed for lower concentrations of H_2SO_4 , so observations were taken for higher (1N, 2N and 3N) concentrations of acid. The results are depicted in Table 2.

The results shown by thermometric methods have same trends as observed in mass loss method. Thus, both methods have good agreement with each other. In this method also the maximum efficiency was shown by *N*-(salicylidine) – 4 – methoxy aniline(SB_3) at the highest concentration (3N) of H_2SO_4 . The variation of reaction number (RN) with inhibitor concentration is depicted graphically for 1.0 N H_2SO_4 in Figure 1. The plots show linear behaviour with negative slope, it means reaction number decreases with increasing inhibitor concentration.

Organic molecules having hetero atoms like N, O and S adsorb on the metallic surface. In the present case Schiff's bases adsorb on the surface of mild steel, thus reduce the exposed surface area for electrochemical reaction. The surface coverage (θ) with increasing concentrations of Schiff's bases are depicted in Table 3. Nitrogen atom present in Schiff's base acts as the reactive centre because of high electron density which results in a monolayer of Schiff's base on the metallic surface.

Table 1. Mass loss ΔM and inhibition efficiency η for Mild Steel in H_2SO_4 solutions with given inhibitor additions

Inhibitor addition ppm	0.1N H_2SO_4 72h		0.5N H_2SO_4 24h		1.0N H_2SO_4 12h		2.0N H_2SO_4 6h	
	$\Delta M, mg$	$\eta \%$	$\Delta M, mg$	$\eta \%$	$\Delta M, mg$	$\eta \%$	$\Delta M, mg$	$\eta \%$
Uninhibited	224.0		127.0		201.0		161.0	
SB ₁								
5	108.0	51.79	54.2	57.32	80.4	60.00	56.3	65.03
10	80.6	64.02	43.1	66.06	63.9	68.20	41.5	74.22
20	65.0	70.98	33.0	74.02	47.8	76.21	23.9	85.15
40	55.0	75.40	22.7	82.12	29.9	85.12	9.1	93.34
SB ₂								
5	120.9	46.02	61.0	51.96	88.0	56.21	59.0	63.35
10	106.0	52.68	51.8	59.21	68.3	66.00	48.3	70.00
20	87.0	61.11	42.0	66.93	50.2	75.02	32.0	80.12
40	67.2	70.00	32.0	74.80	33.0	83.58	17.0	89.44
SB ₃								
5	94.0	57.27	49.5	61.03	72.0	64.18	51.0	68.32
10	76.1	66.02	40.2	68.34	52.0	74.13	35.0	78.26
20	60.4	73.03	30.3	76.14	35.0	85.58	16.1	90.00
40	45.0	79.91	19.0	85.00	21.0	89.55	4.8	97.01
SB ₄								
5	100.8	55.00	52.0	59.05	75.9	62.23	54.1	66.39
10	78.4	65.00	41.6	67.24	61.0	69.63	40.0	75.15
20	62.7	72.01	31.3	75.35	44.2	78.01	20.9	87.39
40	51.0	77.23	20.0	84.25	23.0	88.55	8.1	94.72
SB ₅								
5	125.4	44.04	62.0	51.18	91.8	55.32	64.4	59.87
10	109.0	51.33	53.3	58.03	76.3	62.03	49.9	69.00
20	93.0	58.48	44.0	65.35	56.2	72.13	33.8	79.00
40	68.7	69.33	34.1	73.14	37.5	81.34	22.0	86.33

Table 2. Reaction Number (RN) and inhibition efficiency for Mild Steel in H_2SO_4 solution with given inhibitor additions at $25 \pm 0.01^\circ\text{C}$.

Inhibitor additions	1 N H_2SO_4		2 N H_2SO_4		3 N H_2SO_4	
	RN Kmin^{-1}	$\eta\%$	RN Kmin^{-1}	$\eta\%$	RN Kmin^{-1}	$\eta\%$
Uninhibited	0.0186		0.0362	—	0.0628	
SB ₁						
5	0.0094	49.46	0.0162	55.24	0.0238	62.10
10	0.0074	60.21	0.0144	60.22	0.0219	65.12
20	0.0063	66.13	0.0101	72.08	0.0160	74.52
40	0.0048	74.19	0.0083	77.07	0.0126	79.93
SB ₂						
5	0.0102	45.16	0.0163	54.97	0.0262	58.28
10	0.0084	54.16	0.0152	58.01	0.0231	63.06
20	0.0074	60.22	0.0115	68.23	0.0169	73.09
40	0.0059	68.28	0.0091	74.86	0.0144	77.07
SB ₃						
5	0.0091	51.08	0.0145	59.94	0.0219	65.00
10	0.0070	62.37	0.0127	64.92	0.0200	69.10
20	0.0056	69.89	0.0094	74.03	0.0106	78.98
40	0.0040	78.49	0.0065	82.04	0.0100	85.03
SB ₄						
5	0.0093	50.00	0.0159	56.07	0.0232	63.05
10	0.0071	61.83	0.0134	62.98	0.0201	67.99
20	0.0059	68.28	0.0097	73.20	0.0150	76.27
40	0.0044	76.34	0.0076	79.00	0.0106	83.12
SB ₅						
5	0.0106	43.01	0.0171	52.76	0.0276	56.05
10	0.0087	53.22	0.0156	56.90	0.0243	61.30
20	0.0079	57.53	0.0119	67.12	0.0182	71.01
40	0.0063	66.13	0.0097	73.20	0.0163	74.04

Table 3. Surface coverage (θ) for Mild Steel in H_2SO_4 solutions with given inhibitor additions. Effective area of specimen = 5.0 cm^2

Inhibitor addition ppm	0.1N H_2SO_4 , 72h		0.5N H_2SO_4 , 48 h		1.0N H_2SO_4 , 12h		2.0N H_2SO_4 , 6 h	
	Surface Coverage (θ)	$\log\left(\frac{\theta}{1-\theta}\right)$	Surface Coverage (θ)	$\log\left(\frac{\theta}{1-\theta}\right)$	Surface Coverage (θ)	$\log\left(\frac{\theta}{1-\theta}\right)$	Surface Coverage (θ)	$\log\left(\frac{\theta}{1-\theta}\right)$
SB ₁								
5	0.52	0.0348	0.57	0.1224	0.60	0.1761	0.65	0.2688
10	0.64	0.2499	0.66	0.2881	0.68	0.3274	0.74	0.4542
20	0.71	0.3889	0.74	0.4543	0.76	0.5006	0.85	0.7533
40	0.75	0.4771	0.82	0.6585	0.85	0.7533	0.94	1.1950
SB ₂								
5	0.46	-0.0696	0.52	0.0348	0.56	0.1047	0.63	0.2311
10	0.53	0.0522	0.59	0.1581	0.66	0.2881	0.70	0.3679
20	0.61	0.1943	0.67	0.3076	0.75	0.4771	0.80	0.6021
40	0.70	0.3680	0.75	0.4771	0.84	0.7202	0.89	0.9080
SB ₃								
5	0.57	0.1224	0.61	0.1943	0.64	0.2499	0.68	0.3274
10	0.66	0.2881	0.68	0.3274	0.74	0.4543	0.78	0.5497
20	0.73	0.4319	0.76	0.5006	0.83	0.6886	0.90	0.9542
40	0.80	0.6021	0.85	0.7533	0.90	0.9542	0.97	1.5096
SB ₄								
5	0.55	0.0872	0.59	0.1581	0.62	0.2126	0.66	0.2881
10	0.65	0.2688	0.67	0.3076	0.70	0.3680	0.75	0.4771
20	0.72	0.4102	0.75	0.4771	0.78	0.5497	0.87	0.8256
40	0.77	0.5248	0.84	0.7201	0.89	0.9080	0.95	1.2788
SB ₅								
5	0.44	-0.1047	0.51	0.0174	0.54	0.0696	0.60	0.1761
10	0.51	0.0174	0.58	0.1402	0.62	0.2126	0.69	0.3475
20	0.58	0.1402	0.65	0.2688	0.72	0.4102	0.79	0.5754
40	0.69	0.3475	0.73	0.4319	0.81	0.6297	0.86	0.7883

The presence of electron releasing group $-\text{OCH}_3$ on SB₃ increases the electron density, thus increases the inhibition efficiency. The higher efficiency in higher concentration of H_2SO_4 is may be due to the fact that under strong acidic strength the ionisation of Schiff's base gets enhanced and it favours the adsorption strongly, thus increasing the inhibition efficiency.

Many investigators used Langmuir adsorption isotherm to study the characteristics of inhibitors²¹⁻²². It has been supposed that inhibitors decrease the surface area of metals for electrochemical reaction to take place. Hoar and Holliday²¹ have shown that Langmuir isotherm

$$\log \left[\frac{\theta}{1-\theta} \right] = \log A + \log C - \frac{Q}{2.303 RT}$$

should give a straight line of unit gradient for the plot between $\log \left[\frac{\theta}{1-\theta} \right]$ and $\log C$. A is a constant which is independent of temperature and C is the bulk concentration of the inhibitor. The plots shown in Figure 2 are linear but the gradients are not equal to unity. The deviation may be due to the fact that adsorbed species interact with each other on the metallic surface.

Conclusions

A study of five synthesised bases viz. *N*-(furfurilidine) – 4- methoxy aniline (SB₁), *N*-(furfurilidine) – 4- methylaniline (SB₂), *N*-(salicylidine) – 4- methoxy aniline (SB₃), *N*-(cinnamalidine) – 4 –methoxy aniline (SB₄) and *N*-(cinnamalidine) - 2-methylaniline (SB₅) has shown them to be effective corrosion inhibitors for mild steel in H₂SO₄ acid. Mass loss and thermometric methods have indicated that the inhibition efficiencies increase with increasing strength of acid from 0.1 N H₂SO₄ to 3N H₂SO₄ and with increasing concentration of inhibitors in the range from 5 ppm to 40 ppm.

It has been observed that inhibiting effect has deviation from ideal 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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