A Comparative Study of Inhibitive Effects of Some Schiff Bases on Mild Steel in Acidic Media by Mass Loss Techniques

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Received 8 December 2009; Accepted 5 February 2010

Abstract: Mass loss techniques have been employed to study the corrosion inhibition of some newly synthesized Schiff bases. *viz.* *N*-4-(Diethyl amino) salicylidine-2-amino-5-chloropyridine (SB₁), *N*-(4-ethylbenzalidine)-2-amino-5-chloropyridine (SB₂), *N*-(4-ethylbenzalidine)-2-amino-5-bromopyridine (SB₃), *N*-4-(Diethyl amino) salicylidine-2-amino-5-bromopyridine (SB₄) for mild steel in HCl and H₂SO₄ solutions. Results of inhibition efficiencies from the mass loss technique show that Schiff bases are good inhibitors in both the acidic solutions. Inhibition efficiencies increase with the increase in the concentration of acids as well as those of inhibitors. Maximum efficiency for H₂SO₄ was found 99.78% and for HCl it was 97.92%.

Keywords: Corrosion, Schiff Bases, Corrosion rate, Surface coverage.

Introduction

Mild Steel is an important metal regarding to its wide applications in industry in various mechanical and structural purposes, like in bridgework, industrial parts, steam engine parts, automobiles, for ship hulls and off shore drilling platforms *etc.* Mild steel is passive towards an alkali but it is prone to corrosion in acids like HCl and H₂SO₄ solutions. These acids are generally used for drilling operations, Pickling baths and in descaling processes¹.

Corrosion of mild steel is very common and serious problem, which causes considerable economic loss through out the world. Although it is inevitable but proper maintenance, good design and effective inhibitors may control it. Corrosion of mild steel and its alloys in different acid media has been extensively studied²⁻⁵.

It has been established that the organic compounds having heteroatoms like N, O and S, which have lone pair of electrons, adsorb on the metal surface⁶⁻¹² and thus cause inhibition.

Effects of *N*- and *S*-containing organic compounds such as substituted benzothizoles and various organic *S*-containing compounds of Fe and Mild steel have been studied¹³⁻¹⁵. In the present investigation the inhibition efficiency of four newly synthesized Schiff bases *viz.* *N*-4-(Diethylamino) salicylidine-2-amino-5-chloropyridine (SB₁), *N*-(4-ethylbenzalidine)-2-amino-5-chloropyridine (SB₂), *N*-(4-ethylbenzalidine)-2-amino-5-bromopyridine (SB₃), *N*-4-(Diethylamino) salicylidine-2-amino-5-bromopyridine (SB₄), have been studied for mild steel in HCl and H₂SO₄ solutions.

Experimental

A rectangular specimen of mild steel having dimensions 2.0 cm x 2.0 cm x 0.021 cm containing a small hole of about 0.02 cm diameter near the upper edge were taken. The approximate composition of the specimen was 99.7% Fe, 0.11% C, 0.5% Mg, 0.13% Si, 0.06% S. Specimens were cut from a sheet and thoroughly cleaned by buffing to produce a spotless finish and then degreased. Finally each specimen was washed with acetone and dried. All chemicals used for the synthesis of Schiff bases were of analytical reagent grade and solutions of HCl and H₂SO₄ were prepared in double distilled H₂O. All the Schiff bases were prepared by conventional method *i.e.* by refluxing equimolar quantities of respective aldehydes and amines. Each specimen was weighed accurately with a digital balance up to the accuracy of 0.1 mg and then suspended in a borosilicate glass beaker of 50 mL capacity containing test solution, by a V-shaped glass hook made by capillary tubes at room temperature. After the test, Specimens were cleaned with running H₂O and dried with hot air drier and then weighed again. The Percentage inhibition efficiency (η%) was calculated as¹⁶.

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

Where ΔM_u = Mass loss of specimen in uninhibited solution, ΔM_i = Mass loss of specimen in inhibited solution. The corrosion rate in mm/yr (milli mils per year) can be obtained by following equations¹⁷.

$$\text{C.R (mm/yr)} = \frac{\Delta M \times 87.6}{ATD}$$

ΔM =Mass loss in mg, A =Exposed area of metal surface in cm², T =Time of exposure in hours, D =Metal density in gm/cm³ and 1 mil=0.001 inch. Surface coverage (θ) of metal specimen by inhibitor was calculated as

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

Where ΔM_u and ΔM_i have same significances as given in the formula of inhibition efficiency (η %).

Results and Discussion

Mass loss (ΔM) and percentage inhibition efficiencies (η%) for different concentrations of HCl and inhibitors are shown in Table 1 and those of for the H₂SO₄ are shown in Table 2. It is observed that percentage inhibition efficiency (η%) increases with increase in the concentrations of both the acids and also with the increase in the concentration of inhibitors.

Table 1. Mass loss (ΔM) & inhibition efficiency ($\eta\%$) for mild steel in HCl solution with given inhibitor additions; Temperature: -30 ± 0.1 °C

Inhibitor	N HCl, 88 h		0.5N HCl, 72 h		10 N HCl, 64 h		10 N HCl, 49 h	
Concentration, %	ΔM , mg	$\eta\%$	ΔM , mg	$\eta\%$	ΔM , mg	$\eta\%$	ΔM , mg	$\eta\%$
Uninhibited	21.3	-	37.9	-	43.4	-	153.6	-
SB ₁								
0.1	10.0	53.05	15.2	59.89	13.4	69.12	35.7	76.75
0.3	7.3	65.72	12.4	67.28	10.5	75.80	28.5	81.44
0.5	6.1	71.36	10.2	73.08	8.5	80.41	25.0	83.72
0.7	5.2	75.58	8.4	77.83	5.6	87.09	14.3	90.69
SB ₂								
0.1	8.2	61.50	11.5	69.65	10.6	75.57	26.3	82.87
0.3	6.8	68.07	9.8	74.14	8.8	79.72	19.0	87.63
0.5	5.4	74.64	7.7	79.68	6.6	84.79	12.6	91.79
0.7	3.8	82.15	5.3	86.01	4.3	90.09	6.5	95.76
SB ₃								
0.1	8.1	61.97	9.4	75.19	6.3	85.48	12.4	91.92
0.3	6.9	67.60	7.9	79.15	4.9	88.70	8.1	94.72
0.5	5.6	73.70	6.7	82.32	3.5	91.93	7.3	95.24
0.7	3.8	82.15	4.3	88.65	2.5	94.23	3.5	97.72
SB ₄								
0.1	10.4	51.17	17.6	53.56	17.5	59.67	49.6	67.70
0.3	9.0	57.74	15.4	59.36	15.8	63.59	42.3	72.46
0.5	7.7	63.84	13.0	65.69	13.3	69.35	36.4	76.30
0.7	6.3	70.42	10.8	71.50	11.7	73.04	27.6	82.03

Table 2. Mass loss ΔM & inhibition efficiency $\eta\%$ for mild steel in H₂SO₄ solution with given inhibitor additions. Temperature: -30 ± 0.1 °C

Inhibitor	0.1N H ₂ SO ₄ , 75 h		0.5N H ₂ SO ₄ , 75 h		1.0N H ₂ SO ₄ , 75 h		2.0N H ₂ SO ₄ , 75 h	
Concentration, %	ΔM , mg	$\eta\%$	ΔM , mg	$\eta\%$	ΔM , mg	$\eta\%$	ΔM , mg	$\eta\%$
Uninhibited	23.2	-	32.7	-	49.6	-	93.8	-
SB ₁								
0.1	9.8	57.75	11.2	65.74	13.7	72.37	18.9	79.85
0.3	7.3	68.53	10.4	68.19	10.6	78.62	14.7	84.32
0.5	5.9	74.56	8.5	74.00	8.3	83.26	13.1	86.03
0.7	4.6	80.17	6.4	80.42	4.8	90.32	6.2	93.39
SB ₂								
0.1	8.7	62.50	8.8	73.08	9.2	81.45	11.2	88.05
0.3	5.9	74.56	6.4	80.42	8.3	83.26	4.9	94.77
0.5	5.1	78.01	5.7	82.56	4.8	90.32	4.5	95.20
0.7	3.3	85.77	3.7	88.68	2.8	94.35	3.4	96.37
SB ₃								
0.1	5.2	77.58	5.7	82.56	5.1	89.71	4.0	95.73
0.3	4.3	81.46	4.6	85.93	3.7	92.54	2.7	97.12
0.5	3.2	86.20	3.3	89.90	2.9	94.15	1.0	98.93
0.7	2.3	90.08	1.9	94.18	2.0	95.96	0.2	99.78
SB ₄								
0.1	9.7	58.18	12.9	60.55	16.0	67.74	25.7	72.60
0.3	8.0	65.51	10.7	67.27	13.5	72.78	12.7	86.46
0.5	7.1	69.39	9.6	70.64	11.6	76.61	9.5	89.87
0.7	5.6	75.86	6.3	80.73	8.9	82.05	5.1	94.56

All the four Schiff bases show maximum inhibition efficiency at the highest concentration of both the acids 2 N at their highest concentration i.e. 0.7%. The maximum efficiency was shown by *N*-(4-ethylbenzalidine)-2-amino-5-bromopyridine (SB₃) in HCl (97.72%) and in H₂SO₄ (99.78%).

Corresponding corrosion rate (mm/yr) and surface coverage (θ) for HCl solutions are depicted in Table 3 where as for H₂SO₄ they are shown in Table 4. It is observed from both the tables that corrosion rate of mild steel decreases with the increase in the concentrations of inhibitors where as corrosion rate increases with the increase in the strength of HCl and H₂SO₄ solutions.

Corrosion rate of mild steel is much higher in H₂SO₄ than in HCl. It means H₂SO₄ has more adverse effect on mild steel in comparison to HCl. Values of surface coverage indicate that inhibitors are in general more effective in H₂SO₄ than in HCl. 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 (2N) of acids at maximum concentration (0.7%). Surface coverage (θ) and $\log [\theta/1-\theta]$ values of mild steel in HCl solutions are depicted in Table 5. Where as, for H₂SO₄, these are shown in Table 6. It is observed from both the tables that as Surface coverage (θ) increases, the value of $\log [\theta/1-\theta]$ also increases.

Table 3. Corrosion rate (mm/yr) & surface coverage (θ) for mild steel in HCl solution with given inhibitor additions; Temperature: -30 ± 0.1 °C; Effective area of specimen = 8 cm²

Inhibitor Concentration, %	0.1 N HCl, 88 h		0.5 N HCl, 72 h		1.0 N HCl, 64 h		2.0 N HCl, 49 h	
	C.R (mm/yr)	Surface Cover. (θ)	C.R (mm/yr)	Surface Cover. (θ)	C.R (mm/yr)	Surface Cover. (θ)	C.R (mm/yr)	Surface Cover. (θ)
Uninhibited	0.39	-	0.84	-	10.85	-	5.01	-
SB ₁								
0.1	0.18	0.54	0.34	0.59	3.35	0.69	1.16	0.77
0.3	0.13	0.66	0.27	0.68	2.62	0.76	0.93	0.81
0.5	0.11	0.71	0.22	0.74	2.12	0.80	0.81	0.84
0.7	0.09	0.76	0.18	0.78	1.40	0.87	0.46	0.91
SB ₂								
0.1	0.14	0.64	0.25	0.70	2.65	0.75	0.85	0.83
0.3	0.12	0.69	0.21	0.74	2.20	0.79	0.62	0.87
0.5	0.09	0.75	0.17	0.80	1.65	0.84	0.41	0.92
0.7	0.06	0.82	0.12	0.86	1.07	0.90	0.21	0.96
SB ₃								
0.1	0.15	0.62	0.21	0.75	1.57	0.85	0.40	0.92
0.3	0.12	0.68	0.17	0.79	1.22	0.88	0.26	0.94
0.5	0.10	0.74	0.15	0.82	0.87	0.92	0.24	0.95
0.7	0.07	0.82	0.10	0.89	0.62	0.94	0.11	0.98
SB ₄								
0.1	0.19	0.51	0.39	0.53	4.37	0.59	1.62	0.67
0.3	0.16	0.58	0.34	0.59	3.95	0.63	1.38	0.72
0.5	0.14	0.64	0.29	0.66	3.32	0.69	1.18	0.76
0.7	0.11	0.70	0.24	0.71	2.92	0.73	0.90	0.82

Table 4. Corrosion rate (mm/yr) and surface coverage (θ) for mild steel in H_2SO_4 solution with given inhibitor additions; Temperature: $-30 \pm 0.1^\circ\text{C}$, Effective area of specimen $= 8 \text{ cm}^2$

Inhibitor Concentration, %	0.1N H_2SO_4 , 75 h		0.5N H_2SO_4 , 75 h		1.0N H_2SO_4 , 75 h		2.0N H_2SO_4 , 75 h	
	C.R. (mmpy)	Surface Cover. (θ)	C.R. (mmpy)	Surface Cover. (θ)	C.R. (mmpy)	Surface Cover. (θ)	C.R. (mmpy)	Surface Cover. (θ)
Uninhibited	0.50	-	0.70	-	1.06	-	2.00	-
SB ₁								
0.1	0.21	0.58	0.24	0.65	0.29	0.72	0.40	0.80
0.3	0.15	0.68	0.22	0.68	0.22	0.79	0.31	0.84
0.5	0.12	0.74	0.18	0.74	0.18	0.83	0.28	0.86
0.7	0.09	0.80	0.13	0.80	0.10	0.90	0.13	0.93
SB ₂								
0.1	0.18	0.62	0.19	0.73	0.20	0.81	0.24	0.88
0.3	0.12	0.75	0.13	0.80	0.17	0.83	0.10	0.95
0.5	0.10	0.78	0.12	0.83	0.10	0.90	0.09	0.95
0.7	0.07	0.86	0.08	0.89	0.06	0.94	0.07	0.96
SB ₃								
0.1	0.11	0.78	0.12	0.82	0.10	0.90	0.08	0.96
0.3	0.09	0.81	0.09	0.86	0.07	0.92	0.05	0.97
0.5	0.06	0.86	0.07	0.90	0.06	0.94	0.02	0.98
0.7	0.04	0.90	0.04	0.94	0.04	0.96	0.004	0.99
SB ₄								
0.1	0.20	0.58	0.27	0.61	0.34	0.67	0.55	0.72
0.3	0.17	0.65	0.29	0.68	0.28	0.73	0.27	0.86
0.5	0.15	0.69	0.20	0.71	0.25	0.77	0.20	0.90
0.7	0.12	0.76	0.13	0.81	0.19	0.82	0.11	0.94

Table 5. Surface coverage (θ) and $\log \left[\frac{\theta}{1-\theta} \right]$ for mild steel in HCl solutions with given inhibitor additions Effective area of specimen $= 8 \text{ cm}^2$

Inhibitor Concentration, %	0.1N HCl (88 h)		0.5N HCl (72 h)		1.0N HCl (64 h)		2.0 N HCl (49 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)	$\log \left[\frac{\theta}{1-\theta} \right]$
Uninhibited	-	-	-	-	-	-	-	-
SB ₁								
0.1	0.53	0.53	0.60	0.17	0.70	0.35	0.77	0.52
0.3	0.66	0.28	0.67	0.31	0.76	0.49	0.81	0.64
0.5	0.71	0.40	0.73	0.43	0.80	0.61	0.84	0.71
0.7	0.75	0.49	0.78	0.54	0.87	0.83	0.90	0.99
SB ₂								
0.1	0.61	0.20	0.70	0.36	0.75	0.50	0.83	0.68
0.3	0.68	0.33	0.74	0.46	0.80	0.60	0.88	0.85
0.5	0.75	0.47	0.80	0.60	0.85	0.75	0.92	1.05
0.7	0.82	0.66	0.86	0.79	0.90	0.96	0.96	1.35

Contd..

SB ₃									
0.1	0.62	0.21	0.75	0.48	0.85	0.77	0.92	1.05	
0.3	0.68	0.32	0.79	0.58	0.89	0.89	0.95	1.25	
0.5	0.74	0.45	0.82	0.67	0.92	1.06	0.95	1.30	
0.7	0.82	0.66	0.89	0.89	0.94	1.21	0.98	1.63	
SB ₄									
0.1	0.50	-0.01	0.53	0.062	0.60	0.17	0.68	0.32	
0.3	0.58	0.13	0.59	0.16	0.63	0.24	0.72	0.42	
0.5	0.64	0.25	0.66	0.28	0.69	0.35	0.76	0.50	
0.7	0.70	0.38	0.71	0.40	0.73	0.43	0.82	0.66	

Table 6. Surface coverage (θ) and $\log \left[\frac{\theta}{1-\theta} \right]$ for mild steel in H₂SO₄ solutions with given inhibitor additions. Effective area of specimen = 8 cm²

Inhibitor Concentration, %	0.1 N H ₂ SO ₄ (75 h)		0.5 N H ₂ SO ₄ (75 h)		1.0 N H ₂ SO ₄ (75 h)		2.0 N H ₂ SO ₄ (75 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)	$\log \left[\frac{\theta}{1-\theta} \right]$
Uninhibited	-	-	-	-	-	-	-	-
SB ₁								
0.1	0.58	0.13	0.66	0.28	0.72	0.42	0.80	0.60
0.3	0.68	0.34	0.68	0.33	0.79	0.56	0.84	0.73
0.5	0.74	0.47	0.74	0.45	0.83	0.70	0.86	0.79
0.7	0.80	0.60	0.80	0.61	0.90	1.10	0.93	1.15
SB ₂								
0.1	0.62	0.22	0.73	0.43	0.81	0.64	0.88	0.87
0.3	0.74	0.47	0.80	0.61	0.83	0.70	0.95	1.26
0.5	0.78	0.55	0.82	0.67	0.90	0.97	0.95	1.30
0.7	0.86	0.78	0.89	0.89	0.94	1.22	0.96	1.42
SB ₃								
0.1	0.77	0.54	0.82	0.67	0.90	0.94	0.96	1.35
0.3	0.81	0.64	0.86	0.78	0.92	1.09	0.97	1.53
0.5	0.86	0.79	0.89	0.94	0.94	1.20	0.99	1.96
0.7	0.90	0.96	0.94	1.20	0.96	1.37	1.09	2.66
SB ₄								
0.1	0.58	0.14	0.60	0.19	0.68	0.32	0.73	0.42
0.3	0.65	0.28	0.67	0.31	0.73	0.43	0.86	0.80
0.5	0.69	0.35	0.70	0.38	0.77	0.51	0.89	0.95
0.7	0.76	0.49	0.80	0.62	0.82	0.66	0.94	1.24

Generally the organic molecules containing heteroatoms like oxygen, sulphur and nitrogen cause blockage of active sites on the metallic surface, thus resulting in the decrease in corrosion rate. Nitrogen atom present in Schiff bases has lone pair of electrons and thus Schiff base forms a monolayer on the metallic surface. The presence of -C₂H₅ and -OH groups in Schiff bases further increases the electron density and thus increases the inhibition efficiency of inhibitor. It has been observed that inhibition efficiency is higher in higher concentrations of acids. This may be due to the fact that in strong acidic conditions ionization of Schiff base

increases which favours the adsorption strongly and thus further reduces the exposed area of metal which results further increase in inhibition efficiency.

Langmuir adsorption isotherm plot (graph between $\log C$ and $\log [\theta/1-\theta]$) for mild steel in 0.1N HCl and in 0.1N H₂SO₄ containing the inhibitors as Schiff Bases are shown in Figure 1 and 2.

Figure 1. Langmuir adsorption isotherms for mild steel in 1.0 N HCl

Figure 2. Langmuir adsorption isotherms for mild steel in 1.0 N H₂SO₄

Conclusion

A study of five synthesized bases has shown them effective corrosion inhibitors for mild steel in HCl and H₂SO₄ acid solutions. Mass loss method has shown that efficiencies of inhibitors increase with increase in the concentration of acids as well as those of inhibitors. Among the four Schiff bases under study maximum inhibition efficiency was shown by SB₃ in both acid solutions at 0.7% concentrations at the highest (2 N) strength.

It has been observed that corrosion rate of mild steel is much higher in H₂SO₄ than in HCl which gives the conclusion that H₂SO₄ is much more corrosive for mild steel than HCl. Results of surface coverage indicate that synthesized Schiff bases are more effective in H₂SO₄ than in HCl.

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