Influence of Formazan Derivatives on Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium

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Abstract: Formazan of benzaldehyde (FB) and formazan of *p*-dimethyl amino benzaldehyde (FD) were synthesized. These compounds were studied as corrosion inhibitor for mild steel in 1.11 N hydrochloric acid by weight loss method. The result showed that the corrosion inhibition efficiency of these compounds was found to vary with the temperature and acid concentration. Also, it was found that the corrosion inhibition behaviour of FD is greater than that of FB. The kinetic treatment of the results gave first order kinetics. The relative corrosion inhibition efficiency of these compounds has been explained on the basis of structure dependent - electron donor properties of the inhibitors.

Keywords: Mild steel, Corrosion inhibitors, Weight loss method, Formazan derivatives.

Introduction

Concentrated mineral acids are used extensively in pickling, cleaning, descaling and oil well acidising of metallic materials cause damage of corrosion^{1,2}. It has been speculated that organic inhibitors are more effective with iron and that the polar organic compounds containing sulphur and nitrogen are good corrosion inhibitors for the acidic solutions of metals³.

High electron density of the sulphur and nitrogen atoms in the heterocyclic organic compounds help the organic molecules to get chemisorbed on to the metal surface⁴. Due to the aggressiveness of hydrochloric acid solution against structural materials, such as carbon steel, the use of corrosion inhibitor is usually required to minimize the corrosion attack⁵⁻⁸. Therefore, in this investigation, the corrosion inhibition of mild steel in 1.11N HCl solution in the absence and presence of formazan of benzaldehyde (FB) and formazan of *p*-dimethyl amino benzaldehyde (FD) at various temperatures have been studied by weight loss method.

Experimental

According to ASTM method as reported already,⁹ cold rolled mild steel strips were cut into pieces of 5 cm × 1 cm having the following composition of Fe = 99.686%, Ni = 0.013%, Mo = 0.015%, Cr = 0.043%, S = 0.014%, P = 0.009, Si = 0.007%, Mn = 0.196% and C = 0.017%. They were pickled in pickling solution (5% H₂SO₄) for 3 minutes and washed with distilled water followed by polished with various grades of emery papers and degreased using trichloroethylene. The weight of specimen were noted and then immersed in test solution containing various concentrations of inhibitors at room temperature 303 K, 353 K and 403 K. After the duration of 2 h in hydrochloric acid, the specimens were removed from test solutions and pickled in pickling (5% sulphuric acid) solution, dried and finally weighed. The differences in weights were noted and the corrosion rates were calculated.

Solutions

All the solutions were prepared using NICE brand AR grade chemicals in double distilled water and bubbling purified by nitrogen gas for 30 minutes to carry out de-aeration of the electrolytes. Hydrochloric acid solution was prepared by double distilled water. It was standardized by titrating against sodium carbonate solution and its normality was found to be 1.11 N. The corrosion inhibitor solution of 0.1% formazan of benzaldehyde was prepared by dissolving 0.1 g of formazan of benzaldehyde in 100 mL of test solution. And also, 0.2%, 0.3%, 0.4% and 0.5% solutions of FB were prepared. Similarly formazan of *p*-dimethyl amino benzaldehyde solutions were prepared.

Results and Discussion

The corrosion behaviour of mild steel in hydrochloric acid with FD and FB is given in Figure 1, which was studied by weight loss method at different temperatures (303K, 353K and 403K). From the graph, it is observed that the weight loss of mild steel in the acid decreases with increasing concentration of additives, which suggesting that the additives are corrosion inhibitor for mild steel in 1.11N HCl. From the data of weight lost method, the corrosion rate (CR) was calculated using the equation:

$$CR = (87.6 \times W) / (D \times A \times T)$$

Figure 1 (a) Variation of corrosion rate (CR) with concentration of FB (in %) in HCl solution at different temperature, (b). Variation of inhibition efficiency (IE) with concentration of FB (in %) in HCl solution at different temperature, (c). Variation of corrosion rate (CR) with concentration of FD (in %) in HCl solution at different temperature, (d). Variation of inhibition efficiency (IE) with concentration of FD (in %) in HCl solution at different temperature.

Where W, D, A and T are weight loss (in mg), density of mild steel (7.86 g/cc), area of the specimen in cm square and exposure time in hours respectively.

Similarly, Inhibition efficiency was calculated using the equation,

$$IE \% = [(W_o - W_i) / W_o] \times 100$$

Where W_o and W_i are the values of the weight loss (in g) of mild steel in the absence and presence of inhibitor respectively. The values of corrosion rate and inhibition efficiency in absence and presence of difference concentration of inhibitor used in 1.11 N HCl solution at 303, 353 and 403K for 2 hours were given in Table 1.

Table 1. Corrosion inhibition behaviour of mild steel in 1.11N HCl solution in absence and presence of FB and FD by weight loss measurement.

Corrosion Inhibitors	Conc. of inhibitor, %	Corrosion Rate (mm/y)			Inhibition Efficiency, %		
		303K	353K	403K	303K	353K	403K
FB	Blank	19.84	780.04	958.81	-	-	-
	0.1	11.59	474.67	624.68	41.57	39.15	34.85
	0.2	9.81	418.94	568.73	50.56	46.29	41.84
	0.3	6.13	367.34	513.01	69.10	52.91	46.49
	0.4	4.57	306.49	432.76	76.97	60.71	57.18
	0.5	4.12	249.87	377.04	79.21	67.97	60.67
FD	Blank	19.84	780.04	858.50	-	-	-
	0.1	7.13	307.83	400.44	64.04	60.54	53.36
	0.2	6.46	289.66	374.47	67.42	62.87	56.38
	0.3	5.46	242.18	308.05	72.47	68.95	64.12
	0.4	4.12	182.33	260.46	79.21	76.63	69.66
	0.5	2.90	149.23	248.53	85.39	80.87	71.05

From Table 1, it is clear that the corrosion rate is decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor. In addition, the maximum corrosion inhibition efficiency of FD and FB is 85.39%, 79.21% respectively in 1.11N HCl at 0.5% solution of inhibitor in 303K. And also, it is concluded that FD was best inhibitor in mild steel corrosion in HCl when compared with that of FB.

Kinetic Studies

In addition, the experiment was conducted at different immersion time to study the rate of reaction. The plot of log (weight loss) *versus* immersion time as shown in Figure 2, give a straight line indicating that it follows first order reaction. The values of the rate constant was calculated using the first order rate law¹⁰, $k = (2.303/t) \log([A_o]/[A])$. Here $[A_o]$ is the initial mass of the metal and $[A]$ is the mass corresponding to time 't'.

The half-life ($t_{1/2}$) were calculated using the relationship¹¹, $t_{1/2} = 0.693 / k$. The values of rate constant and half-life ($t_{1/2}$) obtained from the above relations are summarized in Table 2. Half life values are found to be constant at different immersion time. The constant value of the rate constant further confirmed that the corrosion of mild steel in HCl solution in presence of FB and FD follows first order reaction.

Figure 2 (a). Half life plot for weight loss with immersion time in HCl solution in the presence of FB at 303K, (b). Half life plot for log (weight loss) with immersion time in HCl solution in the presence of FB at 303K, (c). Half life plot for weight loss with immersion time in HCl solution in the presence of FD at 303K, (d). Half life plot for log (weight loss) with immersion time in HCl solution in the presence of FB at 303K.

Table 2. Rate constant (k) and half-life values for the corrosion of mild steel at different immersion times in 1.11N HCl solution in absence and presence of inhibitors of different concentration at 303K.

Conc. of Inhibitor %	FB		FD	
	k ($\times 10^{-3}$), h^{-1}	$t_{1/2}$, h	k ($\times 10^{-3}$), h^{-1}	$t_{1/2}$, h
0.1	1.760595 (± 0.059)	393.6	1.16246 (± 0.087)	596.1
0.2	1.578338 (± 0.042)	439.1	0.881029 (± 0.077)	786.6
0.3	1.582695 (± 0.033)	437.9	0.737189 (± 0.078)	940.1
0.4	1.362773 (± 0.016)	508.5	0.578363 (± 0.012)	1198.2
0.5	1.248923 (± 0.011)	554.9	0.446225 (± 0.018)	1553.0

Comparison of corrosion inhibitory behaviour of FB and FD

Since hydrazinecarboxamide and phenylhydrazine groups are basic in nature due to availability of electrons on N atom, it act as adsorption center. Hence, both FB and FD shows goods inhibitory character. However, *N,N*-dimethyl group in phenylmethyldene ring induces more basic nature to FD. Hence the N atom in FD therefore undoubtly has high electron density for adsorption on to the mild steel surface than FB. So, inhibition behaviour of FD increases tremendously when compared to that of FB.

Conclusions

The FB and FD showed good performance as corrosion inhibitor in HCl solution medium due to the presence of heteroatom and unsaturated bond that cause effective adsorption process leading to the formation of an insoluble protective surface film which suppresses the metal dissolution reaction. First order types of reaction were observed in the kinetic studies. The inhibition efficiency increased with increase in concentration of inhibitors for 0.1% to 0.5% and decreased with rise in temperature from 303 K to 404 K. The maximum inhibition efficiency of FB and FD were 79.21% and 85.39% respectively in 1.11 N HCl at 303K (0.5%) for 2 hours of immersion time. From the studies, it was concluded that FD was efficient inhibitor in mild steel corrosion when compared with FB in hydrochloric acid medium.

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