

INFLUENCE OF 2-SALICYLIDENEAMINO-6-METHYL-BENZOTHAZOLE ON
THE CORROSION AND PERMEATION OF HYDROGEN THROUGH MILD STEEL
IN ACIDIC SOLUTIONS

M.A.QURAIISHI, M.A.WAJID KHAN, M.AJMAL

Corrosion Research Laboratory, Department of Applied Chemistry,
Faculty of Engineering and Technology,
Aligarh Muslim University, Aligarh- 202 002 , India

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S.MURALIDHARAN, S.ANGAPPAN

Central Electrochemical Research Institute, Karaikudi
623 006, Tamil Nadu, India

SUMMARY

A new corrosion inhibitor namely 2-salicylideneamino-6-methyl-benzothiazole (SAMEBT) has been synthesised and its inhibiting action on the corrosion of mild steel in 1 M HCl and 0.5 M H₂SO₄ has been investigated by weight loss measurements and potentiostatic polarisation studies. It behaves as a mixed type inhibitor in the above acidic solutions. It has been found to inhibit the dissolution of steel in both acid solutions by blocking the active sites of the mild steel surface. Hydrogen permeation studies and A.C. impedance measurements indicate the improved performance of the compound in HCl. The adsorption of SAMEBT on the steel surface from both acids is found to obey Temkin's adsorption isotherm.

1. INTRODUCTION

A study of organic corrosion inhibitors is an attractive field of research, due to its usefulness in various industries. Most of the commercial inhibitor formulations are found to include aldehydes and amines as essential ingredients [1,2]. Turbina et al. [3] have observed that condensation products of carbonyls and amines which are known as anils or schiff's bases give higher inhibition efficiency than that for constituent carbonyls and amines. Desai and co-workers [4] have studied a few schiff's bases (derived from aromatic aldehydes and amines) as corrosion inhibitors for mild steel in hydrochloric acid. They found that the inhibition efficiency for the investigated schiff's bases is much greater than that for corresponding amines and aldehydes. These observations have actually led to the synthesis of a few anils by condensing a few substituted aminotriazoles and salicylaldehyde, with a view to evaluate their inhibiting properties on the corrosion of mild steel in acidic solutions. All the anils were found to be effective as inhibitors for acid corrosion of mild steel. The inhibition efficiency for all the inhibitors was found to be greater than that for the corresponding amines and salicylaldehyde [5]. In the present investigation the influence of an anil (SAMEBT) synthesized in the laboratory by condensing an aminobenzothiazole and salicylaldehyde on the corrosion of mild steel in 1 M HCl and 0.5 M H₂SO₄ has been studied.

The choice of this compound as an inhibitor is based on two considerations. Firstly, in addition to the presence of a benzothiazole ring, the presence of π -bond of an azomethine group and π -electrons of phenyl groups can induce greater adsorption of the inhibitor molecules on the metal surface. Secondly, the presence of an -OH group can increase the solubility of the inhibitor in the test solutions, leading to a higher inhibition efficiency.

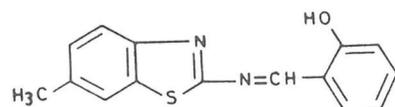
2. EXPERIMENTAL

2.1. Materials and Test Solutions

Mild steel (AISI 1079) strips of size 40 mm X 20 mm X 0.25 mm having composition C = 0.14% , Mn = 0.35% , Si = 0.17% , S = 0.025% , P = 0.03% and remainder Fe , were used for weight loss measurements and hydrogen permeation studies.

For potentiostatic polarisation studies mild steel strips of the same composition with an exposed area of 1 cm² were used. The electrodes were polished successively with emery papers of 1/0, 2/0, 3/0 and 4/0 grade and degreased with trichloroethylene. A.R. grade HCl and H₂SO₄ (MERCK) were used for preparing solutions. Double distilled water was used to prepare solutions of 1 M HCl and 0.5 M H₂SO₄ for all the experiments. The inhibitor namely 2-salicylideneamino-6-methyl-benzothiazole, (SAMEBT) was synthesized in the laboratory following the general

procedure reported elsewhere [6] and the structure of the inhibitor is given below:



Structure of 2-Salicylideneamino-6-methylbenzothiazole

Weight loss measurements were carried out as described earlier [7]. The inhibition efficiency was calculated from weight loss values obtained in the presence and absence of the inhibitor at the end of definite and known intervals of time. Potentiostatic polarisation studies were carried out using EG & G PARC potentiostat/galvanostat (model-173), universal programmer (model-175) and with X-Y recorder (model RK 0089). Hydrogen permeation studies were carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell as described elsewhere [8,9]. Charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were obtained from impedance measurements as described elsewhere [10]. All the experiments were carried out at constant temperature of 35 ± 2 °C. A platinum foil of 3 cm x 3 cm and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively.

3 RESULTS AND DISCUSSION

3.1. Weight Loss Measurements

Table 1 shows the values of inhibition efficiency obtained from weight loss measurements for different concentrations of SAMEBT in 1 M HCl and 0.5 M H₂SO₄. From the calculated weight loss values the inhibition efficiency, P (%), and surface coverage, (θ) of each concentration were calculated using the following equations:

$$P (\%) = \frac{(W_o - W)}{W_o} \times 100 \quad \dots\dots (1)$$

$$\theta = \frac{(W_o - W)}{W_o} \quad \dots\dots (2)$$

where W_o and W are the weight losses in the absence and presence of an inhibitor respectively.

TABLE 1

Inhibition efficiency for different concentrations of SAMEBT for the corrosion of mild steel in 1 M HCl and 0.5 M H₂SO₄ from weight loss data

Conc. of SAMEBT/ppm	Inhibition efficiency/%	
	1 M HCl	0.5 M H ₂ SO ₄
500	97.7	83.4
400	95.6	80.0
300	94.0	77.2
200	91.0	74.0
100	89.1	60.1

It is found from Table 1 that inhibition efficiency increases with increase in the concentration of SAMEBT in test solutions. In general, for the pickling of steel, as pointed by Machu [11], sulphur containing compounds are preferred for H₂SO₄ solution and nitrogen containing compounds for HCl solution. Every and Riggs [12] reported that often a mixture of nitrogen and sulphur compounds is better than either type alone. SAMEBT contains both nitrogen and sulphur atoms. It has exhibited an excellent performance as an inhibitor on the corrosion of mild steel in 1 M HCl and 0.5 M H₂SO₄. It is also found from the table that SAMEBT behaves better in 1 M HCl than 0.5 M H₂SO₄.

The inhibition of corrosion of mild steel in acidic solutions can be attributed to the adsorption of inhibitor molecules on the metal surface. The inhibitor (SAMEBT) can be adsorbed on the metal surface due to following interfacial interactions. (i) Lone pair of electrons of nitrogen and sulphur atoms can interact with the positively charged metal surface. In aqueous acid solution benzothiazole can exist as protonated species [13]. These protonated species can adsorb over negatively charged metal surface through electrostatic force. (ii) π -electrons of benzothiazole and benzene ring can also interact with the positively charged metal surface.

A noteworthy feature of the investigation is that, inhibitor (SAMEBT) gives better performance in 1 M HCl than 0.5 M H₂SO₄. This can be explained by the fact that

chloride ions being less hydrated than sulphate ions, are more strongly adsorbed on the metal surface, by creating, an excess negative charge towards the solution phase which favours synergistic adsorption of inhibitor on the metal surface [14,15]. Similar synergistic mechanism has been proposed by Granese et al. [16] to explain the higher efficiency of some nitrogen containing heterocyclics in acidic solutions.

3.2 Potentiostatic Polarisation Studies

Potentiostatic anodic and cathodic polarisation scans were recorded in 1 M HCl and 0.5 M H₂SO₄ alone and in the presence of different concentrations of SAMEBT. Various electrochemical parameters derived from Tafel plots are given in Tables 2 & 3.

TABLE 2

Electrochemical polarisation parameters for the corrosion of mild steel in 1 M HCl containing different concentrations of SAMEBT

Inhibitor conc./ ppm	$I_{corr}/$ (mA cm ⁻²)	$E_{corr}/$ (mV (SCE))	$b_c/$ (mV dec ⁻¹)	$b_a/$ (mV dec ⁻¹)	Inhibition efficiency/ %
BLANK (HCl)	0.350	-576	110	55	---
500	0.012	-568	98	45	96.57
400	0.015	-574	98	48	95.71
300	0.020	-570	100	50	94.28

TABLE 3

Electrochemical polarisation parameters for the corrosion of mild steel in 0.5 M H₂SO₄ containing different concentrations of SAMEBT

Inhibitor conc./ ppm	I _{corr} / (mA cm ⁻²)	E _{corr} / (mV (SCE))	b _c / (mV dec ⁻¹)	b _a / (mV dec ⁻¹)	Inhibition efficiency/ %
BLANK (H ₂ SO ₄)	0.320	-581	100	50	---
500	0.020	-591	98	46	93.75
400	0.020	-581	95	44	89.06
300	0.070	-581	95	45	78.12

It is seen from Tables 2 & 3, that I_{corr} values decrease significantly in the presence of SAMEBT. This observation indicates that SAMEBT acts as an effective inhibitor for the corrosion of mild steel in both acids. Both cathodic (b_c) and anodic (b_a) Tafel slopes are changed considerably in the presence of 300 ppm SAMEBT, but they remain a constant with increase in the concentration of SAMEBT in both acidic solutions. These observations suggest that the inhibition of corrosion of mild steel in the presence of SAMEBT in 1 M HCl and 0.5 M H₂SO₄ is under mixed control. An inhibitor of this type in both media acts as a mixed type inhibitor. This behaviour brings out the fact that the inhibitor adsorbs by simply blocking the active sites of the steel surface. The mechanisms of both the

anodic and cathodic reactions are not affected. Similar behaviour has been observed during acid corrosion of iron and steel in presence of aliphatic sulphides [17] and thiosemicarbazide [18].

3.3 Hydrogen Permeation Measurements

The importance of the measurements of the hydrogen permeation current for the evaluation of inhibitors with respect to their ability to prevent hydrogen entry into the metal has already been reported [19]. Hydrogen permeation current vs. time curves for mild steel in 1 M HCl and 0.5 M H₂SO₄ alone and in the presence of SAMEBT are shown in Fig. 1.

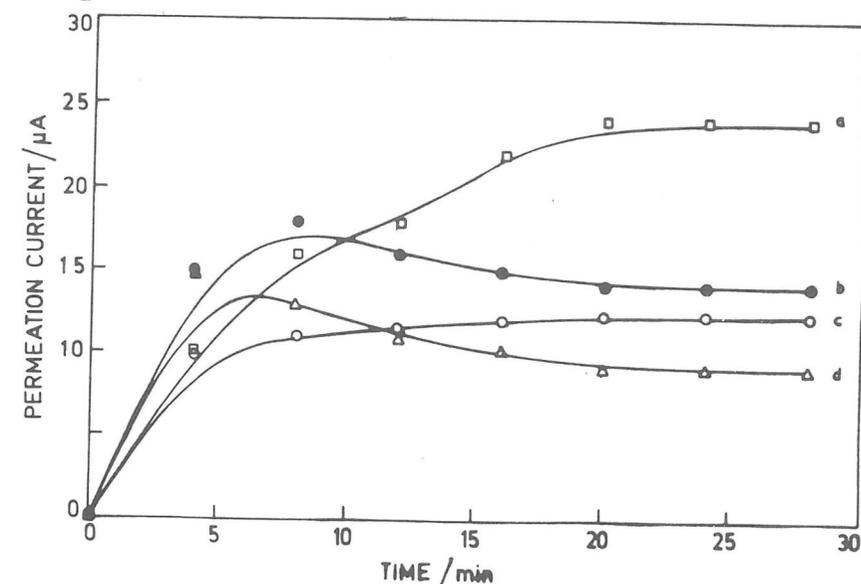


FIG. 1. Hydrogen permeation current vs time curves for mild steel in 1 M HCl and 0.5 M H₂SO₄ containing SAMEBT
 a. 1 M HCl b. 1 M HCl + 300 ppm SAMEBT
 c. 0.5 M H₂SO₄ d. 0.5 M H₂SO₄ + 300 ppm SAMEBT

The permeation current for HCl is almost twice than that for H₂SO₄ solutions due to the stronger adsorption of chloride ions on the metal surface. In the presence of SAMEBT (300 ppm), the permeation current is reduced considerably in both acids. But the extent of reduction is considerably higher in HCl than in H₂SO₄. These observations are in keeping with the facts observed for weight loss experiments. So, in this case a definite correlation is observed between the inhibition efficiency and the amount of hydrogen permeated through steel.

3.4 Electrochemical Impedance Spectroscopy (EIS)

Impedance diagrams obtained for the frequency range 60 kHz to 1 MHz range at the open circuit potential for mild steel in both acids are shown in Figs. 2 and 3.

It is seen from these figures that impedance diagrams are not a perfect semicircle, and this difference has been attributed to frequency dispersion [20,21]. The charge transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru & Haruyama [22]. These values of R_t have been substituted in Stern-Geary equation to obtain the corrosion current. To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of impedance is maximum (-Z''_{max}) is found. Values of C_{dl} are found using the relation

$$C_{dl} = \frac{1}{2\pi f_{max}} \times \frac{1}{R_t} \quad \dots\dots(3)$$

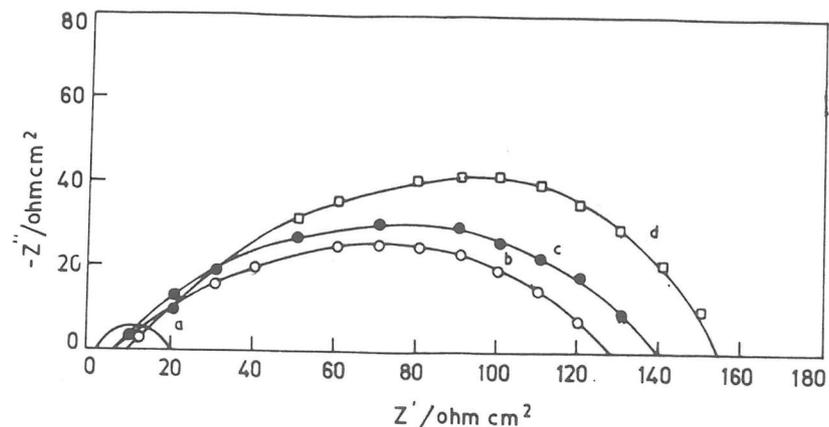


FIG. 2. Impedance spectra for mild steel in 1 M HCl containing SAMEBT

- a. 1 M HCl
- b. 1 M HCl + 300 ppm SAMEBT
- c. 1 M HCl + 400 ppm SAMEBT
- d. 1 M HCl + 500 ppm SAMEBT

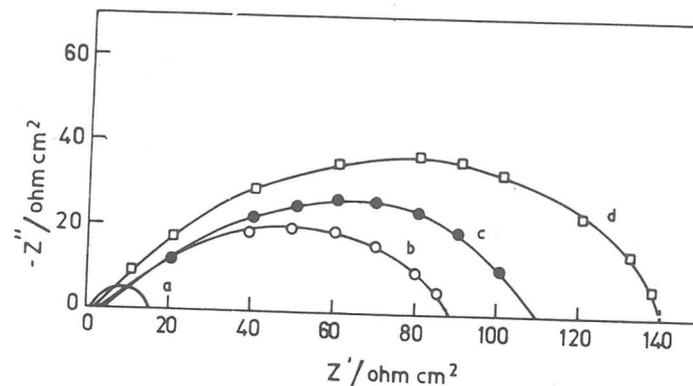


FIG. 3. Impedance spectra for mild steel in 0.5 M H₂SO₄ containing SAMEBT

- c. 0.5 M H₂SO₄ + 400 ppm SAMEBT
- d. 0.5 M H₂SO₄ + 500 ppm SAMEBT

TABLE 4

Impedance parameters for mild steel in 1 M HCl and 0.5 M H₂SO₄ containing different concentrations of SAMEBT

Conc. of SAMEBT/ ppm	1 M HCl			0.5 M H ₂ SO ₄		
	R _t / (ohm cm ²)	I _{corr} / (mA cm ⁻²)	C _{d1} / (μF cm ⁻²)	R _t / (ohm cm ²)	I _{corr} / (mA cm ⁻²)	C _{d1} / (μF cm ⁻²)
BLANK	17.0	0.94	765	13.0	1.11	366
500	143.0	0.09	222	137.0	0.11	185
400	133.0	0.10	280	105.0	0.13	200
300	121.0	0.11	343	84.0	0.16	255

Table 4 gives values of R_t, I_{corr} and C_{d1} for mild steel in 1 M HCl and 0.5 M H₂SO₄, alone and in the presence of different concentrations of SAMEBT. It is seen from this Table that I_{corr} and C_{d1} values are more for HCl than H₂SO₄. The presence of SAMEBT is found to enhance the R_t values from both acids. But C_{d1} values are brought down considerably in both acids, because of its stronger adsorption on the metal surface, which in turn leads to a decrease in the values of I_{corr}.

3.5 Adsorption Isotherm

The surface coverage (θ) values have been obtained from weight loss measurements for various concentrations of SAMEBT. It was observed from Fig.4 that a plot of θ vs. log c gives a straight line in both acid solutions

suggesting that the adsorption of SAMEBT on mild steel/acidic solution interface obeys Temkin's adsorption isotherm.

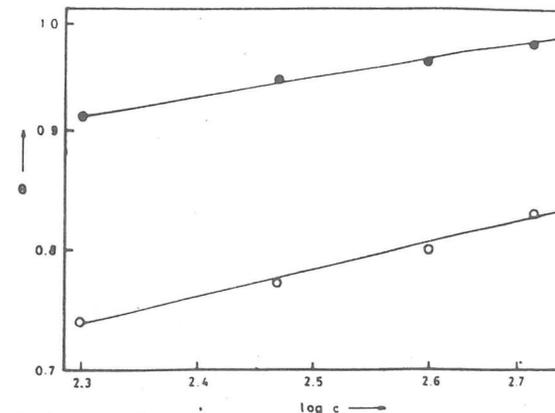


FIG. 4. Temkin's adsorption isotherm plot for mild steel in 1 M HCl and 0.5 M H₂SO₄ containing SAMEBT
a. 1 M HCl b. 0.5 M H₂SO₄

4. CONCLUSIONS

1. SAMEBT has been found to perform well as a corrosion inhibitor in sulphuric and hydrochloric acids, but a better performance is noticed in the case of hydrochloric acid.
2. The mechanism for the inhibition of corrosion of mild steel in the presence of SAMEBT in both 1 M HCl and 0.5 M H₂SO₄ is under mixed control.
3. The compound SAMEBT inhibits the corrosion of mild steel in acidic solutions by a stronger adsorption of inhibitor molecule on the active sites of the steel surface through nitrogen bonding electrons and electrons of the benzothiazole ring and -C = N- group.
4. The compound SAMEBT brings down the permeation current considerably in both acids.

5. The adsorption of SAMEBT on the mild steel surface from both acids obeys Temkin's adsorption isotherm.

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