



Inhibitive effect of N, N-Bis (2-Chloroethylaminobenzaldehyde) ethylthiosemicarbazone on the corrosion of mild steel in 1N H₂SO₄

T.S. Franklin Rajesh¹, A. Sheik Mideen², J. Karthikeyan² and S. Anitha²

¹Department of Chemistry, RMK College of Engineering and Technology, Chennai - 601 206, Tamil Nadu, India

²Department of Chemistry, Sathyabama University, Chennai - 600 119, Tamil Nadu, India

frank_rajesh@yahoo.co.in

Abstract

The inhibitive effect of N, N-Bis (2-Chloroethylaminobenzaldehyde) ethylthiosemicarbazone (BCETSC) on the corrosion of mild steel in 1N H₂SO₄ was investigated by weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The results showed that the inhibition efficiency increases with increase in concentration of the inhibitor. The potentiodynamic polarization curves revealed that BCETSC is a mixed type inhibitor in 1N H₂SO₄. EIS plots indicated that the addition of BCETSC increases the charge-transfer resistance of the corrosion process, and hence the inhibition performance. Scanning electron microscope (SEM) showed that the inhibition occurs due to adsorption of BCETSC molecules at the metal/solution interface. The free energy change value indicated that adsorption of BCETSC molecule is a spontaneous process and it adsorbs physically on mild steel surface.

Keywords: Mild steel, Corrosion inhibition, N, N-Bis (2-Chloroethylaminobenzaldehyde) ethylthiosemicarbazone.

Introduction

The use of inhibitors in acid solutions is one of the most practical methods for the protection of metals against corrosion (Franklin *et al.*, 2010; Stanly *et al.*, 2010). Acid solutions are generally used in several industrial processes. Organic compounds containing functional groups with hetero atoms, which can donate lone pair electrons, are found to be very effective inhibitors against corrosion in acidic environments. Many N-heterocyclic compounds with polar groups and/or n-electrons are effective corrosion inhibitors in acidic solutions. Organic molecules of this type can be adsorbed on the metal surface and form a bond between the N-electron pair and/or n-electron cloud and the metal, thereby reducing the corrosion in acidic solutions. The inhibition efficiencies of organic compounds containing different donor atoms is in the sequence S > N > O [3–5]. Schiff bases have been reported as effective corrosion inhibitors for mild steel (Kaan & Orhan, 2004; Aytac *et al.*, 2005; Emel *et al.*, 2008; Prabhu *et al.*, 2008; Behpour *et al.*, 2009; Franklin *et al.*, 2010; Stanly *et al.*, 2010; Khaled *et al.*, 2010; Saravana *et al.*, 2011; Poornima *et al.*, 2011). These substances generally become effective by adsorption on the metal surface. The present work describes the investigation of inhibitive action of BCETSC on corrosion of the mild steel in 1N H₂SO₄ solution using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The choice of this compound was based on molecular structure considerations.

Experimental details

Materials

Mild steel samples of the composition C=0.058%, Mn=0.252%, P=0.004%, S=0.002% and Fe = 99.684% were used for the measurement of the corrosion rates. Rectangular specimens of working surface area 5 × 2.5 ×

0.16 cm² were used for the weight loss method. These specimens were polished mechanically using emery papers of different grades and washed thoroughly with triple distilled water, degreased with acetone and dried at room temperature.

Inhibitor

The compound N, N-Bis (2-Chloroethylaminobenzaldehyde) ethylthiosemicarbazone was synthesized in the laboratory by the condensation reaction of N, N-Bis (2-Chloroethylaminobenzaldehyde) with the appropriate ethylthiosemicarbazide in ethanol media (Ashassi *et al.*, 2005). The aggressive electrolyte solution of 1N H₂SO₄ (Sigma-Aldrich analytical grade) was prepared with double distilled water. The structure of N, N-Bis (2-Chloroethylaminobenzaldehyde) ethylthiosemicarbazone (BCETSC) is shown in Fig.1. The BCETSC was used in concentrations 1×10⁻⁴M, 2.5×10⁻⁴M, 5×10⁻⁴M and 7.5×10⁻⁴M in 1N H₂SO₄.

Weight loss method

There are many experimental techniques, which can be used to evaluate the inhibitor efficiencies. Weight loss is one of the simplest and frequently used methods (Derya *et al.*, 2008). 100 ml of 1N H₂SO₄ without inhibitor was used as blank test solution. The mild steel specimens were immersed in hanging position in blank and the different concentrations of inhibitor solution for 2 hours. After the corrosion test, the mild steel specimens were carefully washed in double distilled water, dried and then weighed. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. The inhibition efficiency (η_w) has been assessed using a known relation (1) reported elsewhere (Lukovits *et al.*, 2005; Ashassi *et al.*, 2005):

$$\% \eta_w = \left(\frac{w - w'}{w} \right) \times 100 \quad (1)$$



Table 1. Weight loss data of mild steel in 1N H₂SO₄ for various concentrations of BCETSC

Inhibitor concentration	Corrosion rate (mg.cm ⁻² .min ⁻¹)	Inhibition efficiency (%)
1N H ₂ SO ₄ (Blank)	12.1 × 10 ⁻²	-
1N H ₂ SO ₄ + 1.0 × 10 ⁻⁴ M BCETSC	4.74 × 10 ⁻²	61.25
1N H ₂ SO ₄ + 2.5 × 10 ⁻⁴ M BCETSC	3.13 × 10 ⁻²	74.25
1N H ₂ SO ₄ + 5.0 × 10 ⁻⁴ M BCETSC	1.76 × 10 ⁻²	85.55
1N H ₂ SO ₄ + 7.5 × 10 ⁻⁴ M BCETSC	8.08 × 10 ⁻³	93.35

where, w and w' are weight losses in the absence and presence of inhibitor respectively.

Electrochemical methods

Electrochemical measurements were conducted in a conventional three electrode system. A platinum electrode as counter electrode, mild steel sample as working electrode and saturated calomel electrode (SCE) as the reference electrode were used in the electrochemical studies (Ashassi *et al.*, 2005). Tafel polarization curves were obtained with a scan rate of 5mV/s in the potential range from -250 to +250 mV relative to the open circuit potential. All the potentials were reported versus SCE, corrosion current density values were obtained by Tafel extrapolation method (Bommersbach *et al.*, 2005). The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range 1Hz to 100 kHz at the rest potential by applying a 5mV sine wave AC voltage. The double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were calculated from Nyquist plots as described elsewhere (Canan *et al.*, 2007).

SEM analysis

Scanning electron microscopy (JOEL-SEM, S-3400) was used to study the surface morphology of the specimen used. Polished mild steel specimens were tested in plain 1N H₂SO₄ solution and maximum inhibitor concentration 7.5 × 10⁻⁴ M in 1N H₂SO₄ solution. Then the samples were washed with distilled water, dried, and were subjected to scanning electron microscopic examination.

Results and discussion

Weight loss method

The corrosion rate and percentage inhibition efficiency

Fig.1. Structure of N, N-Bis (2-Chloroethylaminobenzaldehyde) ethylthiosemicarbazone

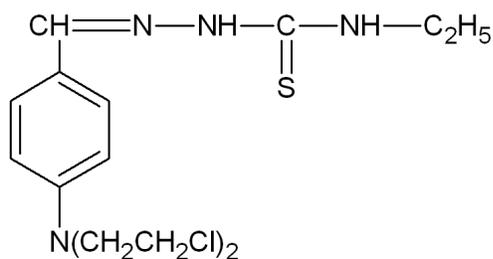
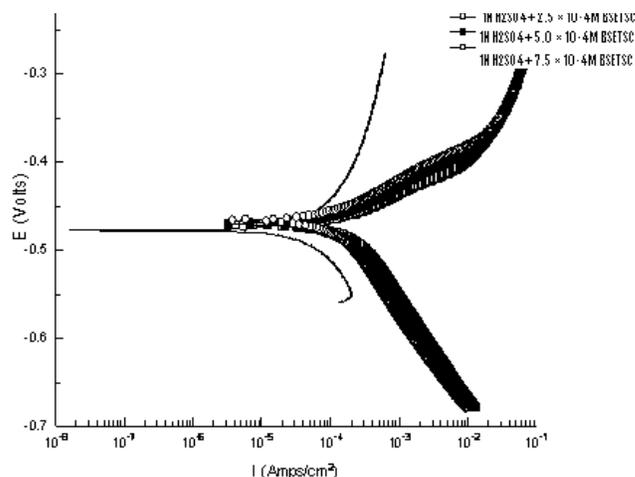


Fig 2. Tafel plot for mild steel corrosion in 1N H₂SO₄ containing different concentrations of BCETSC



calculated from the weight loss results for 2 h are given in Table 1. The coupons immersed in BCETSC inhibitor solutions showed the reduced corrosion rate to a significant extent and thereby showing higher inhibition efficiencies. It can be seen that the inhibition efficiency increases with increase in concentration of BCETSC which suggests that inhibition is a result of adsorption of inhibitor on the metal surface and BCETSC acts as an adsorption inhibitor (Sorkhabi *et al.*, 2005). The reason for the high inhibition efficiencies of BCETSC towards mild steel may be due to the presence of nitrogen and sulphur atoms in BCETSC molecule.

Polarization Technique

Fig. 2 shows the polarization curves recorded for mild steel in 1N H₂SO₄ solution with and without the various concentrations of BCETSC at a scan rate of 5mV.s⁻¹. The percentage of inhibition efficiency ($\% \eta_{pol}$) of BCETSC was calculated using the relation (2):

$$\% \eta_{pol} = \left(\frac{i_{corr} - i'_{corr}}{i_{corr}} \right) \times 100 \quad (2)$$

where, i_{corr} and i'_{corr} are uninhibited and inhibited corrosion current densities respectively (Bommersbach *et al.*, 2005; Lagrenée *et al.*, 2002). The surface coverage degrees (θ) values were calculated using the equation (3):

$$\theta = \frac{i_o - i'}{i_o} \quad (3)$$

where, i_o and i' were respectively, the uninhibited and the inhibited corrosion current densities.

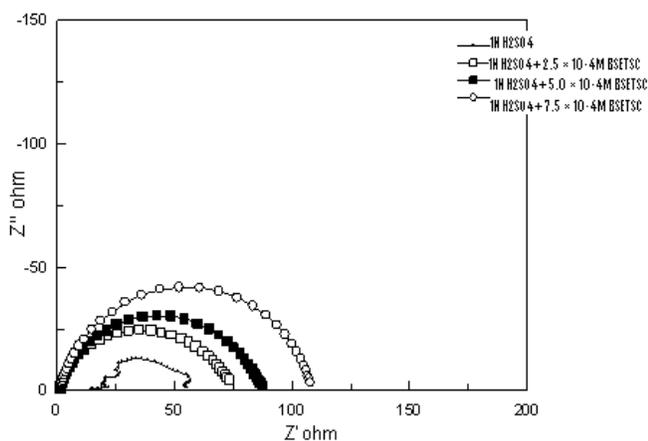
The Tafel plot illustrates that the addition of BCETSC inhibitor decreases the corrosion current densities (i_{corr}). The results obtained from the Tafel plot further indicated that BCETSC inhibits H₂SO₄ corrosion of mild steel via their adsorption on both anodic and cathodic active sites

Table 2. Potentiodynamic polarization parameters of mild steel in 1N H₂SO₄ for various concentrations of BCETSC

Inhibitor concentration	E _{corr} , V (vs SCE)	i _{corr} (A.cm ⁻²)	Surface coverage, θ	Inhibition efficiency (%)
1N H ₂ SO ₄ (Blank)	-0.529	3.6 × 10 ⁻³	-	-
1N H ₂ SO ₄ + 2.5 × 10 ⁻⁴ M BCETSC	-0.4715	2.251 × 10 ⁻⁴	0.3747	93.74
1N H ₂ SO ₄ + 5.0 × 10 ⁻⁴ M BCETSC	-0.4702	1.643 × 10 ⁻⁴	0.5436	95.43
1N H ₂ SO ₄ + 7.5 × 10 ⁻⁴ M BCETSC	-0.4662	1.371 × 10 ⁻⁴	0.6191	99.61

without modifying the mechanism of corrosion reaction. This means that the adsorbed inhibitor molecules block the surface active sites and decrease the area available for hydrogen evolution and metal dissolution reactions (El-Mehdi *et al.*, 2003). The values of corrosion potential (E_{corr}), corrosion current density (i_{corr}), surface coverage (θ) and the percentage of inhibition efficiency (I.E %) were calculated from the Tafel line and listed in Table 1. It is clear that at high concentration of the inhibitor, the values of corrosion potentials (E_{corr}) remain almost unchanged and indicate that the prepared BCETSC inhibitor acts mainly as mixed type inhibitor (Table 2).

Electrochemical impedance studies

Fig. 3. Typical Nyquist plots for mild steel corrosion in 1N H₂SO₄ containing different concentrations of BCETSC

The Nyquist plot for mild steel corrosion in 1N H₂SO₄ containing different concentration of BCETSC is shown in Fig 3. To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum (-Z''_{max}) was determined from the equation (4):

$$f(-Z''_{\max}) = \frac{1}{2\pi C_{dl} R_p} \quad (4)$$

The inhibition efficiency (η_{EIS}) has been assessed using a known relation (5):

$$\eta_{EIS} (\%) = \left(\frac{R_{ct} - R'_{ct}}{R_{ct}} \right) \times 100 \quad (5)$$

Where, R_{ct} and R'_{ct} denote charge transfer resistance of electrode with and without inhibitor respectively.

From the Table 3, it can be noted that when the concentration of inhibitor increases double layer capacitance (C_{dl}) value decreases. Decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the BCETSC molecules function by adsorption at the metal/solution interface. The increase in polarization resistance and the decrease in double layer capacitance were attributed to the enhanced adsorption of the inhibitor molecule on the metal surface. Hence, the corrosion inhibition of mild steel in 1N H₂SO₄ by BCETSC under study may be deduced on the basis of adsorption. In acidic solution, BCETSC can exist as cationic species which may be adsorbed on the cathodic sites of the mild steel and reduce the evolution of hydrogen. Moreover, the adsorption of BCETSC on anodic sites occurs through lone pairs of electrons of sulphur atom of ($\text{C}=\text{S}$) group, which is the center of thiosemicarbazone compound.

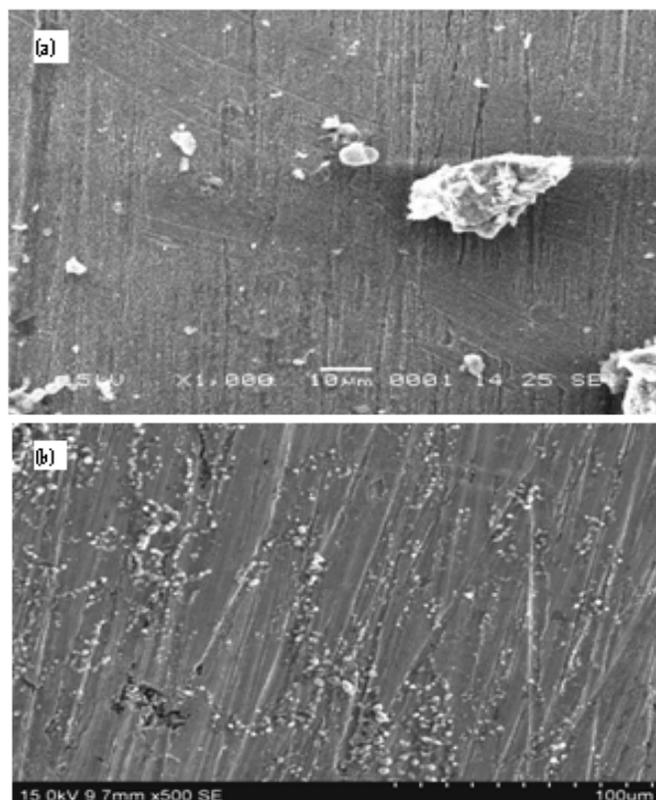
Fig 4. SEM image of (a) corroded Mild Steel sample by 1N H₂SO₄ (b) inhibited Mild Steel sample by 7.5 × 10⁻⁴ M BCETSC in 1N H₂SO₄



Table 3. Electrochemical impedance parameters for mild steel corrosion in 1N H₂SO₄ with various concentrations of BCETSC

Inhibitor concentration	R _{ct} (Ω cm ²)	C _{dl} (μF)	Inhibition efficiency (%)
1N H ₂ SO ₄ (Blank)	23.00	1.045	-
1N H ₂ SO ₄ + 2.5 × 10 ⁻⁴ M BCETSC	72.35	8.9×10 ⁻⁵	68.21
1N H ₂ SO ₄ + 5.0 × 10 ⁻⁴ M BCETSC	84.77	9.3×10 ⁻⁵	72.86
1N H ₂ SO ₄ + 7.5 × 10 ⁻⁴ M BCETSC	107.32	7.8 ×10 ⁻⁵	78.56

SEM study

The surface morphology of mild steel in 1N H₂SO₄, and with 7.5×10⁻⁴M BCETSC were studied by using SEM (Fig. 4a,b). This establishes the interaction of inhibitor molecules with metal surface. The SEM micrographs revealed that the mild steel specimen immersed in inhibitor solution was in better condition having smooth surface while the metal surface immersed in 1N H₂SO₄ solution was rough covered with corrosion products and appeared like full of pits and cavities. These indicated that the above inhibitors hindered dissolution of the mild steel by forming protective adsorbed film on the metal surface and thereby reduce the corrosion rate.

Adsorption Isotherm

Since the corrosion inhibition process is based on the adsorption of Schiff base molecules on the metal surface, the adsorption requires the existence of attractive forces between the adsorbate and the metal surface. It is important to know the type of adsorption and adsorption isotherm that fits the experimental results. The most frequently used adsorption isotherms are Langumir, Temkin and Frumkin. Efficient adsorption on mild steel may be due to either the electronegative donor atoms N and S or the n electron of the aromatic system. Plot of the data calculated from equation (6) showed that the investigated compound agreed with the Langmuir

adsorption isotherm (Kaan *et al.*, 2006; Desai *et al.*, 1986):

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (6)$$

where, K_{ads} is the adsorption equilibrium constant and θ is the coverage degree. When we plot C against C/ θ , we get a straight line (Fig 5).

The adsorption equilibrium constant (K_{ads}) related to the free energy of adsorption (ΔG_{ads}^o) was calculated by equation (7) reported by elsewhere (Vishwanathan & Haldar, 2008; Derya *et al.*, 2008):

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^o}{RT}\right) \quad (7)$$

The value 55.5 is the concentration of water in solution in moles.litre⁻¹, R is gas constant and T is absolute temperature. Negative values of ΔG_{ads}^o are the characteristic feature of strong spontaneous adsorption of the Schiff base compounds on metal surfaces, in turn reflect the high values of inhibition. Moreover, ΔG_{ads}^o values <40 kJ.mol⁻¹ for the Schiff base molecules on metal surface indicate that the compounds follow physical adsorption (Brinic *et al.*, 1995; Ashassi *et al.*, 2004).

The adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG_{ads}^o) for the mild steel with BCETSC solution are given in Table 4. These values show that the number of active sites is nearly constant and approximately equal to those which have been reported by other researchers (Ebenso *et al.*, 1999; Lagrenee *et al.*, 2002). This behavior can be discussed on the basis of the adsorption process that takes place by the occupation of one active site per singly inhibitor molecule. The larger the values of the equilibrium, constant will provide the better inhibition efficiency.

Fig 5. Plot of C against C/ θ for BCETSC

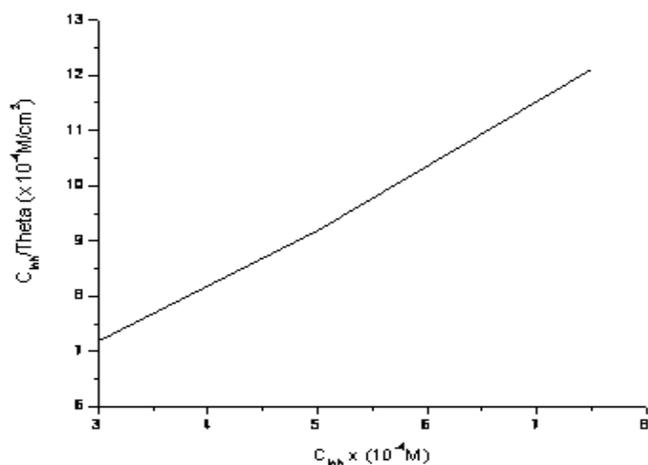


Table 4. Equilibrium constant and free energy of adsorption for mild steel with BCETSC

Inhibitor	Equilibrium constant, K	Free Energy Change, kJ.mol ⁻¹ .
BCETSC	1.52×10 ⁴	- 14.683

Conclusion

The N, N-Bis (2-Chloroethylaminobenzaldehyde) ethylthiosemicarbazone (BCETSC) was found to be effective inhibitor for mild steel corrosion in 1N H₂SO₄ solution. The inhibition efficiency of BCETSC increases with increase in its concentrations. Tafel polarization study has shown that the BCETSC suppresses both anodic and cathodic process and thus acts as mixed type inhibitor. Electrochemical Impedance Spectroscopy study indicated that the addition of inhibitor increases the charge transfer resistance of the corrosion process, and

hence the inhibition performance. Further the results derived from Nyquist plot shows that the BCETSC adsorbs on the mild steel surface through the thiocarbonyl sulphur atom, nitrogen atom as well as π -electrons of the aromatic structure. The scanning electron microscopy of inhibited surface revealed that the BCETSC inhibitor hindered dissolution of the mild steel by forming protective adsorbed film on the metal surface and thereby reduces the corrosion rate. The adsorption mechanism obtained from the results further reveal that the BCETSC follows Langmuir adsorption isotherm and it can adsorb firmly on the mild steel surface by donating electrons to iron atoms.

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