Chemical treatment of zinc surface and its corrosion inhibition studies

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Abstract. The surface treatment of zinc and its corrosion inhibition was studied using a product (BTSC) formed in the reaction between benzaldehyde and thiosemicarbozide. The corrosion behaviour of chemically treated zinc surface was investigated in aqueous chloride–sulphate medium using galvanostatic polarization technique. Zinc samples treated in BTSC solution exhibited good corrosion resistance. The measured electro-chemical data indicated a basic modification of the cathode reaction during corrosion of treated zinc. The corrosion protection may be explained on the basis of adsorption and formation of BTSC film on zinc surface. The film was binding strongly to the metal surface through nitrogen and sulphur atoms of the product. The formation of film on the zinc surface was established by surface analysis techniques such as scanning electron microscopy (SEM–EDS) and Fourier transform infrared spectroscopy (FTIR).

Keywords. Corrosion; inhibitors; electrochemical measurement; zinc.

1. Introduction

Zinc is an important metal with numerous industrial applications and is mainly used for the corrosion protection of steel (Barcelo *et al* 1988; Lin *et al* 1991; Rajendran *et al* 1997; Bozzini *et al* 1999). The zinc coated steel materials provide a greater resistance to corrosion, but when exposed to humid atmosphere, it undergoes rapid corrosion with the formation of corrosion products known as white rust. This is generally observed on galvanized materials and renders the plated zinc materials unsuitable for industrial applications. The formation of the white rust on zinc surface is prevented by the application of chromate treatment (Muller *et al* 2004). The effluent obtained during chromate treatment induces the environmental pollution. But recent environmental regulations restrict the use of chromate solution and recommended its replacement with other non-toxic and, non-polluting agents (Hinton and Wilson 1989). Therefore, there is a need for change in the formulation of corrosion inhibition by an increasing demand for reduced environmental impact.

The zinc or zinc-coated materials treated with a solution of organic compounds provided effective corrosion protection. These compounds containing nitrogen and sulphur elements are capable of forming thin film or molecular layers on the metal surface (Abdel Aal *et al* 1983; Lakhan Jha *et al* 1991; Maja *et al* 1993; Rajappa and Venkatesha 2003). The role of this film is to isolate the corroding

metal from the corrosive medium (Praveen *et al* 2007). This reduced the formation of white rust. Several chelating agents showed corrosion inhibition of zinc. These substances form stable, almost insoluble films with zinc surface through their electro active groups and acts as protective coatings (Leroy and Zavorski 1977; Leroy 1977).

In the present investigation, a compound, BTSC, was synthesized and used for anticorrosion of zinc. This synthesized molecule contains nitrogen and sulphur atoms and favours the formation of a film on zinc surface. The inhibition effect was studied in aqueous corrosive solution using polarization technique. The mechanism of corrosion inhibition was explained on the basis of formation of protective layer on the zinc surface.

2. Experimental

The pure zinc plate (Cu = 0·185, Al = 0·006%, Fe = 0·004%, Mn = 0·3%, Sn = 0·003%, Pb = 0·002%, Cd = 0·002% and the rest zinc) was selected and coupons of desired shapes (5 cm × 1 cm × 4 mm) were prepared. These samples were polished with SiC papers of different grit sizes (200–1200). The electrodes were degreased with trichloroethylene vapours to remove oil and grease. The samples were rinsed with ethanol, followed by distilled water wash. The prepared samples were immersed in the treatment solution for different time intervals.

Benzaldehyde thiosemicarbazone (BTSC) was synthesized from the addition reaction followed by loss of water between benzaldehyde and thiosemicarbozide (Morrison

and Boyd 1973). The purity of the compound was monitored by TLC and then characterized by IR studies. The chemical structure of the BTSC compound is given in figure 1. The zinc specimens were degreased and their surface activated by dipping in 10% HCl for 1 min. The activated zinc surface was water washed before subjecting it into surface treatment process. The concentrations of 2%, 4% and 6% BTSC solution were prepared in ethanol and used as zinc treatment solution. The zinc specimens were immersed in these solutions for different immersion periods (1–3 h) at room temperature. After the treatment, the zinc samples were washed with water and dried in air. The treated samples were subjected to electrochemical studies.

The electrochemical investigations were performed in aqueous solutions of 0·2 M NaCl + 0·2M Na$_2$SO$_4$ by means of a galvanostatic technique. A conventional three-electrode cell consisting of zinc sample (exposed surface area, 1 cm^{-2}) as working electrode, saturated calomel and platinum were used as reference and counter electrodes, respectively. The anodic and cathodic polarization curves for the treated and untreated zinc electrodes were taken using a potentiostat/galvanostat (Elico CL 95). Anodic and cathodic polarization potentials were recorded in the current density range of 0–10 mA/cm^2.

The surface morphology of the treated and untreated zinc samples was investigated by scanning electron microscopy using a SEM–JSM–850 (Jeol) machine with EDS link. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using KBr pellets to characterize the reaction product and scrapped compound of the corroded surface.

3. Results and discussion

3.1 *Electrochemical investigation*

Figure 2 gives the cathodic and anodic polarization curves for treated and untreated zinc. Curve 1 of cathodic polarization exhibits two diffusion plateaus for untreated zinc. This was due to reduction of dissolved oxygen. The oxygen reduction (first plateau) occurs in the vicinity of the corrosion potential through a more or less porous layer. This layer consists of corrosion products and it is formed during the short preliminary hold time at the free corrosion potential. At higher cathodic over potentials the whole surface becomes active, hence oxygen reduction at higher rate takes place (at the layer solution interface) resulting in an increase in current density (second plateau) (Deslouis *et al* 1984).
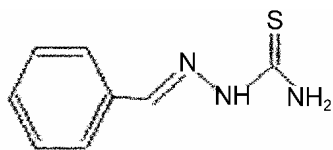
The corrosion of untreated zinc in aerated chloride–sulfate solution was found to be cathodically controlled (Deslouis *et al* 1989). The corrosion current density was obtained by extrapolation of Tafel lines. The corrosion current density, I_{corr} and corrosion potential, E_{corr}, were found to be 89 μA cm^{-2} and –1005 mV, respectively.

The polarization curves of the zinc samples treated at 298 K for 3 h in 2% and 4% BTSC solutions (curves 2 and 3) are also presented in figure 2. The corrosion potential of treated zinc shifted positively by 20–40 mV in comparison to untreated zinc. The zinc samples treated in 4% BTSC solution exhibited higher corrosion resistance, indicating that the surface exposed to the corrosive medium is less active, due to the improvement of the surface coverage by the compound. Further the cathodic curves 2 and 3 revealed that the second plateau of curve 1 progressively disappears with the concentration of BT solution. This indicated a basic modification in the cathodic behaviour of zinc metal. The second plateau of curve 1 becomes almost linear in curve 3. This may result from the formation of porous layer during the preliminary hold time at the free corrosion potential and decreasing the electron transfer rate. In this case, I_{corr} and E_{corr} were obtained by extrapolation of the linear part of the cathodic polarization curves. Further the E_{corr} values indicated that the treated zinc surface is relatively more noble than untreated zinc.

The percentage inhibition efficiency (%IE) was calculated using the relation,

$$\%\text{IE} = \frac{I_{corr} - I_{corr}^1}{I_{corr}} \times 100,$$

where I_{corr} and I_{corr}^1 denote the corrosion current densities for the untreated and treated zinc.

Table 1 shows the values of E_{corr}, I_{corr} and %IE of the treated and untreated zinc. The values of E_{corr} shifted to-

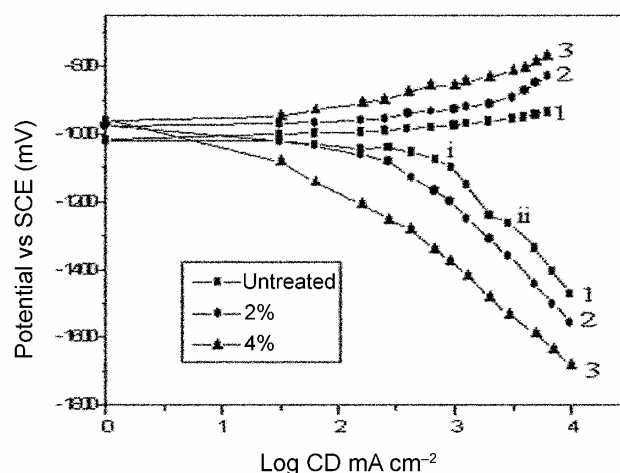**Figure 1.** Structure of BTSC compound.

Figure 2. Polarization curves for treated and untreated zinc.

wards noble direction and the values of I_{corr} were found to decrease in treated zinc surface. The %IE was greater in 4% BTSC than in 2% solution for the same immersion period. The concentration of BTSC is increased to 6% and the percentage inhibition efficiency was found to be slightly increased. Therefore, 4% BTSC solution was taken as optimum concentration.

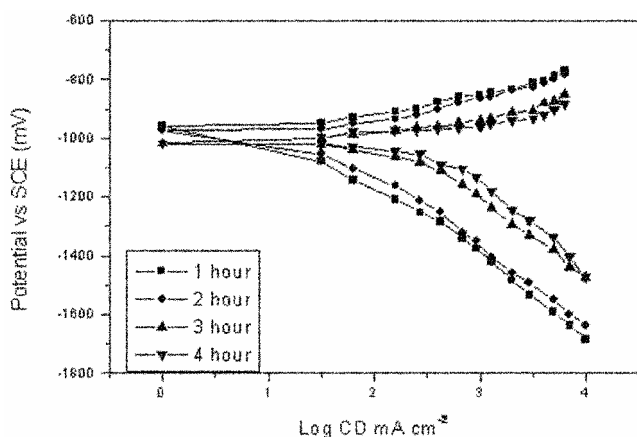### 3.2 *Effect of treatment time*

Figure 3 shows the cathodic and anodic polarization curves of zinc at different treatment times. Figure 4 shows the influence of immersion time on percentage inhibition efficiency. The inhibition efficiency was gradually increased with increase in immersion period up to 3 h in 4% BTSC solution. The increase in the inhibition efficiency values was related to the progressive formation of a protective film on the electrode surface. The inhibition efficiency after 3 h was stabilized and reached a maximum value of 88%.

3.3 *Effect of temperature*

Figure 5 shows the cathodic and anodic polarization curves of zinc at different temperatures. The zinc specimens were treated in 4% BTSC solution for 3 h and sub-

jected to corrosion study at different temperatures. The %IE was decreased regularly with rise of temperature. The decrease of %IE was more at temperature, 308 onwards. Therefore, the formation of protective film is more predominant at relatively low temperature. The variation of %IE with temperature is shown in figure 6.
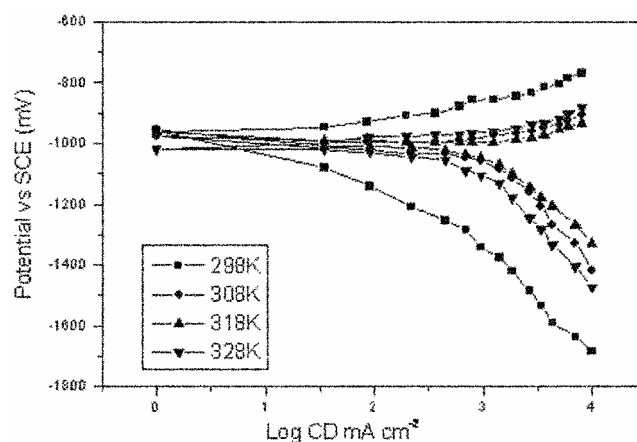
4. Surface analysis techniques

Surface analysis technique was carried out to confirm the formation of a protective film on the zinc surface and also to investigate the establishment of chemical bonds between the electro active groups (–NH, –SH) of the compound with zinc surface. The following techniques were used.

4.1 *SEM–EDS examination*

Scanning electron microscopic study was performed to investigate the change of morphology of the zinc surface.
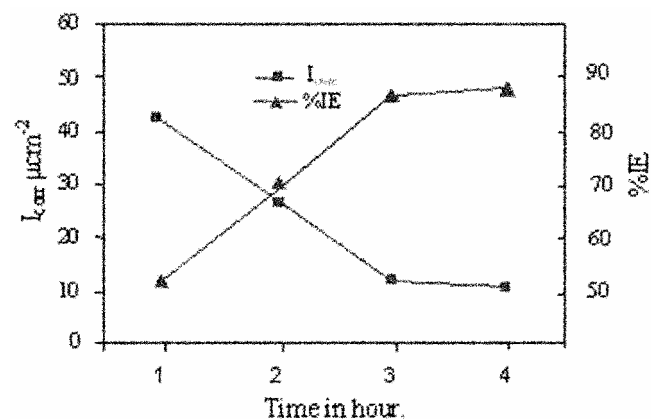
Figure 4. Influence of immersion time on percentage inhibition efficiency.

Table 1. Values of I_{corr}, E_{corr} and %IE of treated zinc for 3 h at 298 K.

Conc. of inhibitor	E_{corr} (mV)	I^1_{corr} (μA cm^{-2})	%IE
Blank	−1005	89 (I_{corr})	−
2%	−975	27	69
4%	−962	12	87
6%	−960	11	88

Figure 3. Cathodic and anodic polarization curves of zinc at different intervals of time.

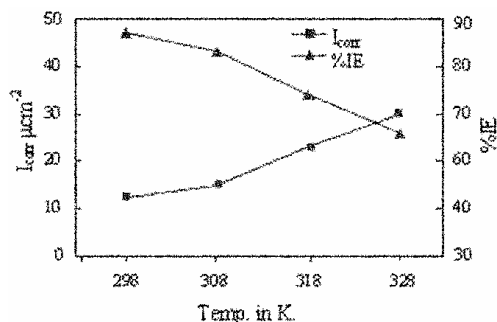**Figure 5.** Cathodic and anodic polarization curves of zinc at different temperatures.

Figure 6. Temperature effect on I_{corr} and % IE of treated zinc.
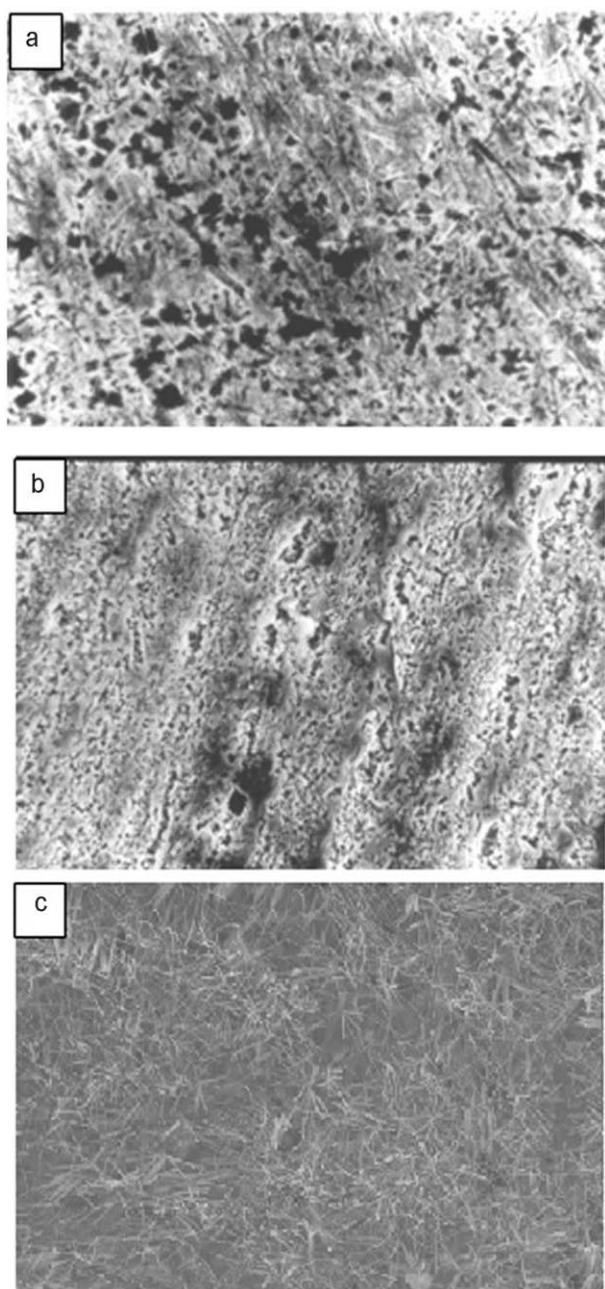

Figure 7. SEM micrographs of **a**. anodic polarized untreated zinc surface, **b**. anodic polarized treated zinc surface and **c**. treated zinc surface.

Figure 7a shows the photomicrograph taken after 10 min of anodic polarization in 0·2 M NaCl + 0·2 M Na$_2$SO$_4$ solution at 298 K. The surface contained small cavities, which are distributed over the entire surface and a needle-like deposit (corrosion product) was observed. In the case of treated sample taken after 10 min of anodic polarization, needle type of deposit was not observed (figure 7b). The surface shows only a few pits covered with corrosion products. This indicates a film of BTSC which hindered the dissolution of metal during anodic polarization. So less pits and corrosion products were noticed. Figure 7c showed a passive film, which was not subjected to the corrosion process.

4.2 *EDS studies*

Figure 8a shows the EDS spectra of corroded zinc surface. Chloride peak was observed due to the possible formation of zinc salts of chloride around the anode sites of the corroding surface. For the treated zinc, the chloride peak was not observed and the observed sulphur signal originated from the BTSC molecule as shown in figure 8b. This observation inferred that the molecule interacted strongly with the metal through sulphur atom.
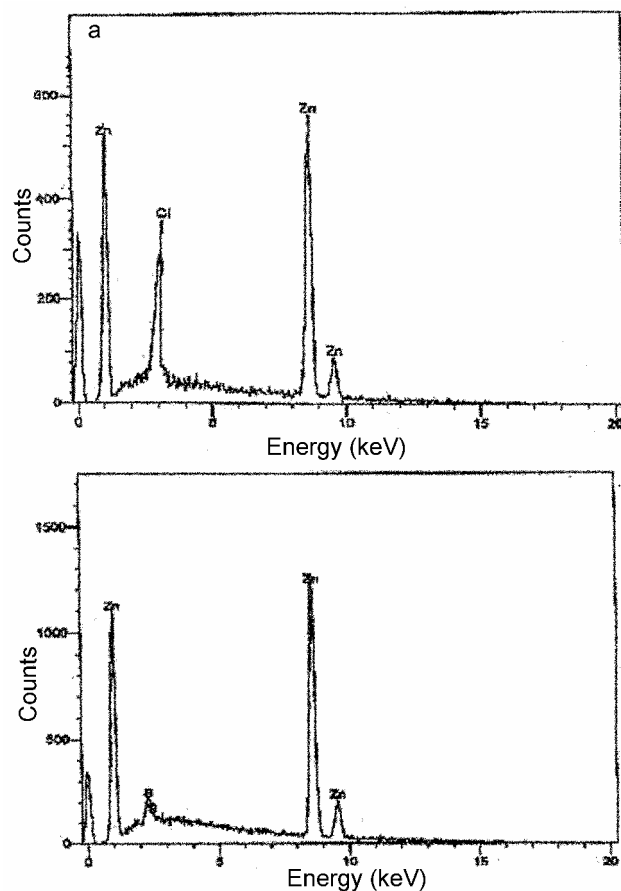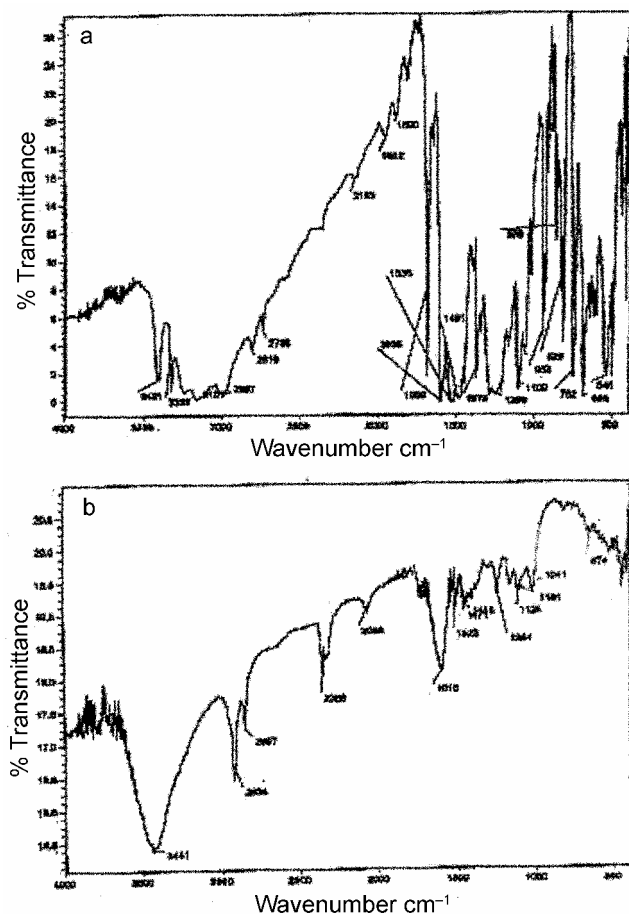

Figure 8. EDS spectra of **a**. corroded untreated zinc and **b**. corroded treated zinc.

Figure 9. FTIR spectra of **a**. BTSC powder and **b**. scrapped BTSC powder from treated zinc surface.

4.3 *FTIR study*

The FTIR spectra were taken to study the establishment of chemical bonds between the zinc surface and BTSC molecule. Figure 9a shows the IR spectrum of BTSC molecule. The characteristic bands at 3421 and 3333 cm^{-1} were attributed to stretching vibrations of the NH$_2$ group, 1605 cm^{-1} corresponds to C=N bond and 2153 cm^{-1} corresponds to aromatic protons. The IR spectrum of scrapped film after anodic polarization is shown in figure 9b. In this spectrum, C=N stretching frequency is shifted to 1616 cm^{-1}, NH$_2$ stretching frequency, 3333, is merged and 3421 is shifted to 3441 cm^{-1} and also this spectrum shows several modifications. These changes in the ab-

sorption frequencies of IR spectra supported the interaction between functional group of BTSC with surface of metal.

5. Conclusions

Electrochemical study showed that zinc treated with BTSC molecule has good corrosion resistance in aqueous chloride–sulphate solution. Maximum inhibition efficiency of 87% was obtained in 4% BTSC solution at 298 K. The treatment induced a basic modification in the cathodic behaviour of zinc and controls the corrosion by decreasing the electron transfer rate. The SEM photographs showed the formation of a passive film on the treated zinc surface. The spectral data confirmed the formation of a stable film and it is strongly attached to the zinc surface through the establishment of chemical interactions with N and S atoms. The synthesized BTSC molecules modified the zinc metal surface and provided good corrosion protection.

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