

ROLE OF THIOUREA ON THE ELECTROCHEMICAL BEHAVIOUR OF ZINC GLYCINE COMPLEXES

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ABSTRACT

Electrochemical behaviour of zinc-glycine complex has been studied in the presence of thiourea on platinum by cyclic voltammetric technique. The obtained results revealed that zinc-glycine complex undergoes successive reduction to zinc with the formation of monovalent zinc complex in a slow step. Thiourea in the plating bath solution hindered both the deposition and dissolution processes. Hydrogen evolution reaction was hindered by the adsorption of thiourea, which strengthened the $M-H_{ads}$ bond and raised the hydrogen over voltage.

Key words: Cyclic voltammetry, Zinc-glycine complexes, Hydrogen evolution, Thiourea

INTRODUCTION

Zinc coating is extensively used world over to protect iron and mild steel from corrosion. Extensive literature is available on the subject [1]. Recent trend on industrial zinc plating is to develop non-cyanide plating bath solutions, which are economical and eco-friendly [2-4]. Many zinc complexes have been tried in zinc plating baths to hinder hydrogen evolution, which is reduced over a wide range of potentials to improve current efficiency and throwing power [5]. An attempt has been made to get good quality zinc coating using glycine and thiourea as additives in the plating bath solution [6]. The subject of basic understanding on the role of additives during electroplating is still in its infancy. Cyclic voltammetric technique has become a powerful tool in understanding the role of additives during electro-deposition of metals [7].

The present communication reports the results pertaining to the study of electrochemical behaviour of zinc-glycine complex and the hydrogen evolution reaction in

the presence of thiourea by cyclic voltammetric technique.

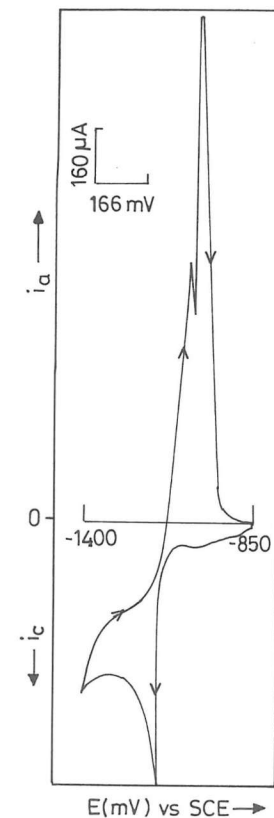
EXPERIMENTAL

All solutions were prepared by using AR grade chemicals and double distilled water. An all glass three electrodes cell assembly of 50mL capacity was used for the voltammetric studies. A platinum wire (0.05cm^2), a large platinum foil and saturated calomel electrode were used as working, counter and reference electrodes respectively. The platinum electrodes were pre-cleaned by the regular procedure [8]. To minimise IR drop a finely drawn capillary was used. The desired potentials were swept (5-100 mV/sec) using a potentiostat (EG&G model 362, USA) and the response was recorded on X-Y recorder (Omnigraphic 2000x). Experiments were carried out at 298 ± 1 K in solutions containing zinc sulphate (0.02M), sodium sulphate (0.02M) and glycine (GY) of desired concentrations ($0.01 < C < 0.04$ M) along with thiourea in the concentration range ($10^{-3} < x < 10^{-2}$ M). The pH of the solution was maintained at 5.0 using dilute sulphuric acid. The experiments were repeated to ensure reproducibility.

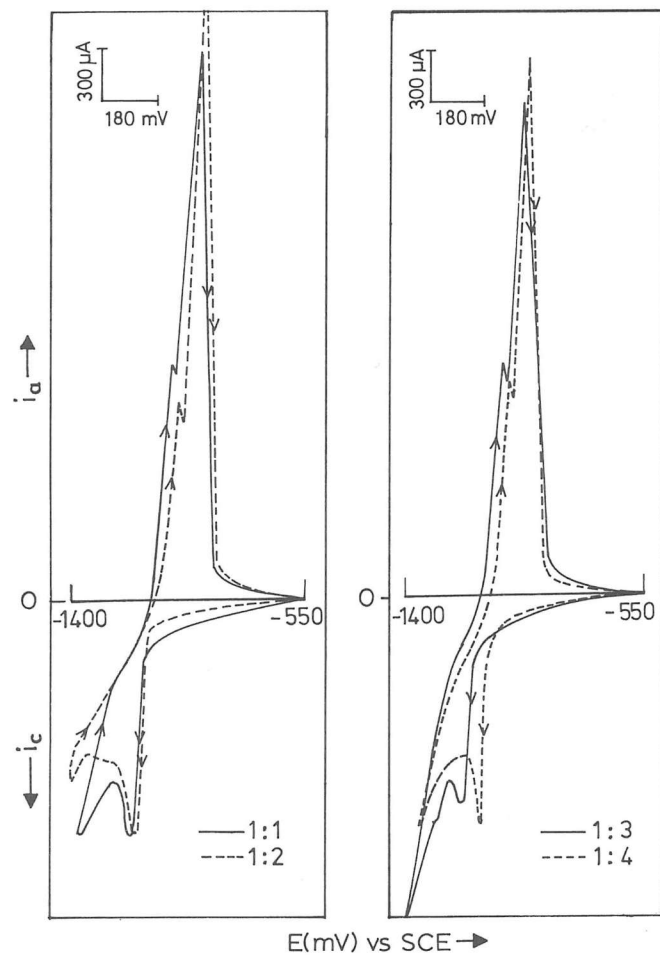
RESULTS

Fig. 1 represents the cyclic voltammogram obtained on platinum in solution containing ZnSO_4 (0.02M) and Na_2SO_4 (0.02M), when polarized from -850 to -1400 mV at 5 mV/s sweep rate. The forward scan (5 – 50 mV/s) exhibited cathodic peaks at -1195 ± 40 mV followed by hydrogen evolution. The reverse scan revealed the independence of peak potential on the sweep rate. The $dE_{p,c}/d\log v$ was found to be 80 mV/decade.

Addition of GY modified the cyclic voltammogram (Fig. 2) when polarized from -550 to -1400 mV. The forward scan exhibited a cathodic peak at -1127 mV followed by hydrogen evolution. The reverse scan exhibited a small peak at -923 mV (I) followed by a peak at -891 mV (II). The anodic peak potential (I) was invariant with sweep rate while that of anodic peak (II) varied as 30 mV/decade with the change of sweep rate. Increase of GY concentration did not modify the spectrum. On the reverse scan the anodic peak potential (I) became active with glycine concentration while that of anodic peak (II) was nearly invariant.



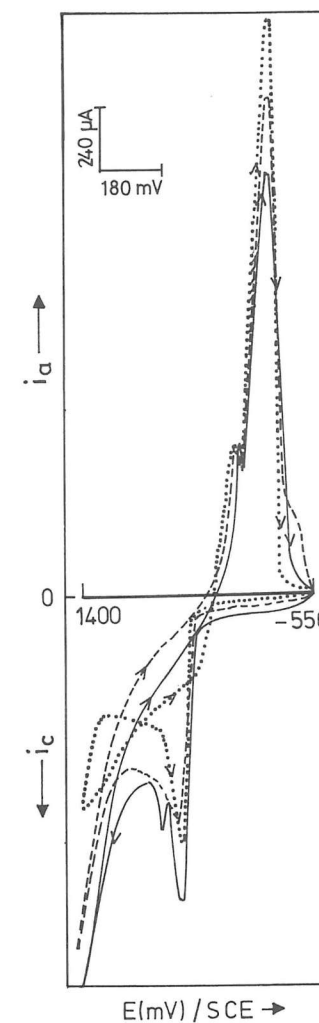
1. Cyclic voltammogram in 0.02M zinc sulphate + 0.02M sodium sulphate at 5 mV/s sweep rate.



2. Cyclic voltammogram in 0.02M zinc sulphate + 0.02M sodium sulphate at 5 mV/s -
Effect of various zinc:GY ratio

This suggests that the dissolution of deposited zinc occurs stepwise and the monovalent zinc species is stabilized by glycine.

Introduction of thiourea to a solution containing zinc ions and GY slightly modified the spectrum (Fig.3). When polarized from -550 mV to -1400 mV, a sharp peak appeared at -1115 mV in 0.001M thiourea solutions. A plateau around -1300 mV followed this. The

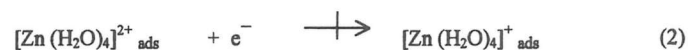


3. Cyclic voltammogram in 0.02M zinc sulphate + 0.02M sodium sulphate + 0.02 M glycine at 5 mV/s - Effect of thiourea concentration
[___ 0.01 M; ---- 0.05 M; 0.001M]

cathodic peak splitting occurred in presence of 0.005M thiourea solution. The reverse scan exhibited an anodic peak at -1012 mV and -890 mV. The anodic and cathodic peak potentials were found to vary with thiourea concentration:

DISCUSSION

In the absence of complexing agents under transient conditions, the deposition of zinc may involve monovalent zinc ion.



By considering the discharge step (2) as slow and irreversible we could write [9,10]

$$E_{p,c} = E^\circ + [\ln K^\circ / D^{1/2} - 0.5 \ln \alpha_c F \Delta\phi / RT - 0.78] \quad (I)$$

Where $E_{p,c}$ is the cathodic peak potential; v is the sweep rate; D is the diffusion coefficient of the Zn^{2+} ions, α_c is the cathodic transfer coefficient and $\Delta\phi$ is the interfacial potential difference. The plot of $E_{p,c}$ vs $\log v$ would give a cathodic Tafel slope. The obtained slope value of 140 ± 10 mV/decade suggests that first electron transfer is the slowest one.

Zinc exists as $\{\text{Zn}(\text{GY})(\text{H}_2\text{O})\}$. The gradual variation of cathodic peak current with the GY concentration reveals that zinc-GY complexes undergo successive reduction as.



For the discharge of divalent complex with the adsorbed monovalent zinc species it can be shown that

$$I_o = K_2 K_1 \{ \text{Zn}(\text{GY})_2(\text{H}_2\text{O})_2 \} \exp -F \Delta\phi / RT \quad (II)$$

A plot of $E_{p,c}$ vs. $\log v$ gave a straight line with a slope of 60 ± 10 mV/decade confirming the above points. Polarographic studies [11] on the reduction of zinc ions without and with complexing agents are in conformity of these findings.

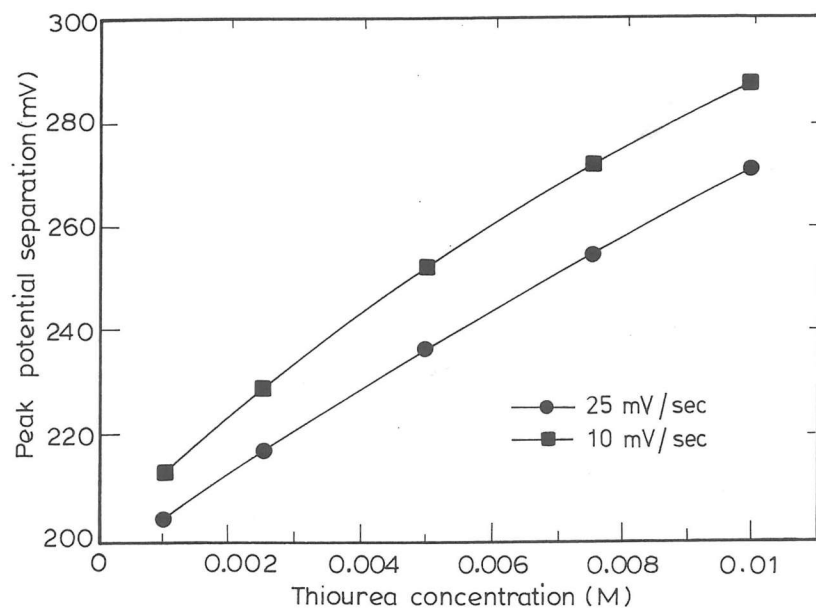
The addition of thiourea to a solution containing different ratios of zinc and GY did not modify the electrochemical spectrum (Table 1). However, the increase in thiourea concentration shifted the cathodic peak potential to more negative value suggesting thiourea offered inhibition to the growth of zinc nuclei. A linear variation of ΔE_p (peak potential separation) with thiourea concentration suggested that thiourea hinders both deposition and dissolution processes (Fig. 4).

Table I: Parameters derived from cyclic voltammogram – Effect of thiourea

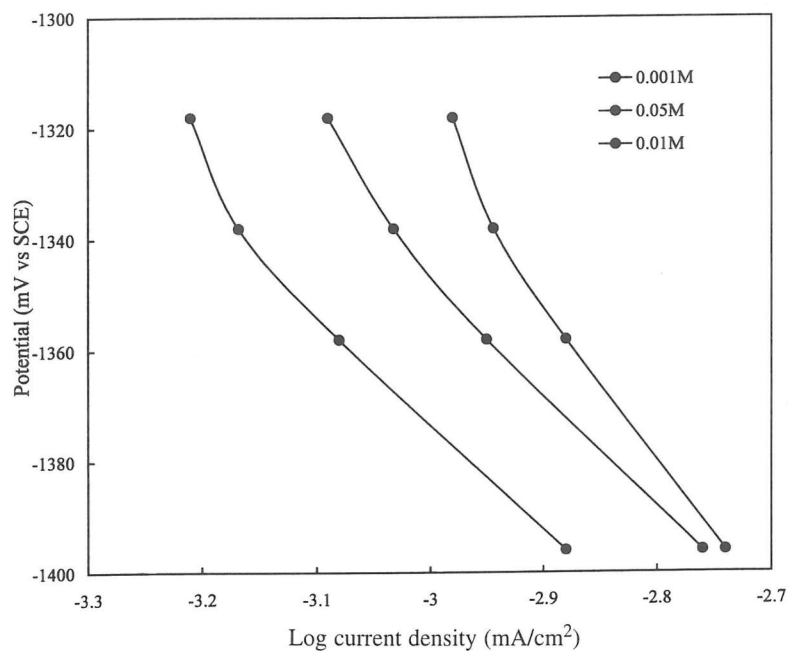
Thiourea concentration (M)	Zinc discharge potential (mV)	Cathodic Peak potential Vs SCE		
		(5mV/sec)	(10mV/sec)	(25mV/sec)
0	-1155	-1100	-1100	-1115
0.001	-1155	-1115	-1120	-1120
0.005	-1155	-1128	-1136	-1145
0.01	-1155	-1150	-1150	-1150

The E-log I curve obtained at 10 mV/sec for hydrogen evolution reaction in presence of thiourea and zinc-GY complex is shown in Fig.5. Thiourea hindered the hydrogen evolution reaction and thereby favored the discharge of zinc complex over a wide range of potentials.

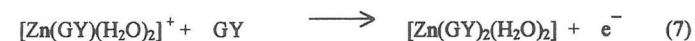
The splitting of anodic peak and the dependence of anodic peak potentials and currents on GY concentration suggest that the dissolution of zinc takes place in succession.



4. Variation of peak potential separation with thiourea concentration



5. E - log current density plot for hydrogen evolution - Effect of thiourea concentration



The interaction of adsorbed organic compounds and the d-band of the platinum could lower the Pt-H bond [12], which reflects the increase in activation energy of the over voltage.

CONCLUSIONS

Voltammetric studies carried out on Zinc-GY complexes revealed that under transient conditions the complex adsorbs and a non-activated interaction between adsorbed molecules hinder the electronation and the first electron transfer is the slow step. Thiourea does not affect the discharge potential of the zinc complex but hinders the growth of the zinc nuclei and the dissolution of the deposited zinc. Thiourea adsorbed and hindered the hydrogen evolution reaction by strengthening the M-H bond and raised the over voltage.

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**Use of 1-phenylamino-3-(4-phenylthiosemicarbazone)-
butane-1,3-dione derivatives as corrosion inhibitors for
C-steel in acidic chloride solutions**

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Abstract

The corrosion inhibition of nitrogen, oxygen and sulphur containing compounds in acidic chloride solutions was studied by chemical and electrochemical techniques. The percentage inhibition efficiency was calculated from both methods is in good agreement. The corrosion rate was found to be a function of the nature, concentration and temperature of the medium. The increase in temperature was found to increase the corrosion rate. The inhibitors are adsorbed on the C-steel surface according to the Langmuir isotherm. Some thermodynamic functions were computed and discussed. Quantum data were calculated and the results of HOMO and LUMO showed that the increase in energy of HOMO corresponds to an increase in the inhibition efficiency.

Key words: Corrosion, C-steel, acid chloride solution, butane-1,3-dione derivatives.

Introduction

As known that the economic power of a country is determined by its output of steel, since progress in the principal economic branches be it mining, transport, manufacturing engineering or agriculture is unthinkable without steel. So, studies of steel properties in general and electrochemical, especially, have been received a great attention. In such respect, the corrosion and corrosion inhibition of steel in the different media become very interesting and important, owing to its wide applicability in industry and domestic life. Numerous studies on iron and steel were done including the corrosion nature and its mechanism in different media. Corrosion inhibition using different inhibitors and the various factors affecting on it were studied by many authors [1-17]. The object of this work is undertaken to investigate the role played by some 1-phenylamino-3-(4-phenylthiosemicarbazone)-butan-1,3-dione derivati-