Cyclic voltammetric studies on zinc(II), NTA complexes on glassy carbon electrodes

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In zinc solutions the deposition involves adsorbed intermediates and these would conform to the Langmuir isotherm. $Zn^{++} + e \longrightarrow Zn^{+}$ and $Zn^{+} + e \rightleftharpoons Zn$. When nitrilo triacetic acid (NTA) is added, the deposition of zinc might take place in a single step, while the dissolution may undergo successive oxidation via monovalent zinc and NTA anion may stabilize the monovalent species.

Key words: Cyclic voltammetry, Zn-NTA complex, glassy carbon electrode

INTRODUCTION

The Zn/Zn^{++} reaction is one of the extensively studied reactions. In noncomplexing solutions a reversible two electron transfer process was observed and multiple polorographic waves associated with various complexes were noticed in complexing solutions [1].

EXPERIMENTAL

A three electrode electrochemical cell consists of glassy carbon as working electrode, platinum as auxillary electrode and SCE as reference electrode. Detailed description of the electrode preparation and cyclic voltammetric set up are presented elsewhere [2].

RESULTS AND DISCUSSION

Figure 1 presents the experimental spectrum obtained in deoxygenated 10^{-3}M ZnSO$_4$ solutions when polarised from -200 to -1600 mV vs SCE. The charge flow corresponding to these peaks was found to inverse with sweep rate, while an increase of scan number increased, the charges under peaks (I) and (II) indicating them to be coupled. Below 5×10^{-2}M, the cathodic (I) and anodic peak potentials (II) varied with sweep rate. The cathodic peak potential (II) was invariant with ν pointing to the possibility of hydrogen evolution reaction. Above 5×10^{-3}M, the $E_{p,a}$ did not vary with ν while the $E_{p,c}$ varied linearly with $\log \nu$. $E_{p,a}$ and $E_{p,c}$ were found to vary linearly with ν. The plot of $E_{p,c}$ vs $\log \nu$ gave a slope of 120 mV/decade and (d $\log i_{p,c}$/d $\log \nu$) at constant Zn^{++} concentration gave a value 0.33. The deposition of zinc ions under the conditions of ν may thus be associated with an adsorption on the surface obeying Langmuir isotherm [2]. It was shown that

$$E_p = \frac{RT}{\alpha F} \ln\left(\frac{-\alpha F}{K_i RT}\right) + \frac{RT}{\alpha F} \ln \nu$$

$$i_p = \frac{(1 - \theta)\alpha Fr\nu}{RT}$$

where the net $i_{Faradaic}$ would be (rd θ/dt) and (RT/α F) the Tafel slope. Plots of $E_{p,c}$ vs $\log \nu$ and $i_{p,a}$ and $i_{p,c}$ are found to give linear curves. The deposition of zinc under transient conditions with adsorbed intermediates following Langmuir isotherm may suggest $Zn^{++} + e \longrightarrow Zn^{+}_{ads}$; $Zn^{+}_{ads} + e \rightleftharpoons Zn$. This is substantiated by the plot of [d $\log i_{p,c}$/d $\log (Zn^{++})$] at constant pH and for different ν giving a value of 0.9.
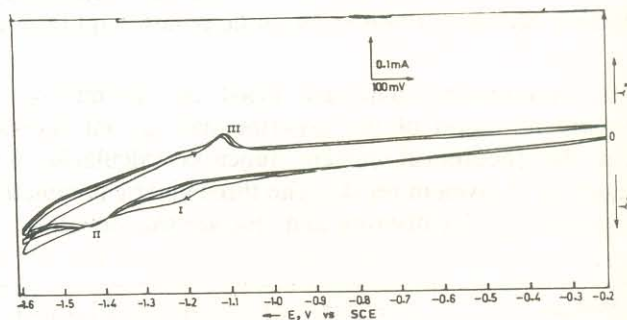

Fig. 1: Typical voltammogram in deoxygenated 10^{-3} M ZnSO$_4$ and 10^{-1} M Na$_2$SO$_4$ at 80 mV/sec for five scans $E_{\lambda,a} = -200$ mV; $E_{\lambda,c} = -1800$ mV

NTA COMPLEXES

Figure 2 presents the electrochemical spectrum obtained with ZnSO$_4$ containing 5×10^{-3}M NTA. When the zinc concentration was increased from 5×10^{-3}M [Fig. 3] the forward scan exhibited a peak at -1275 mV (I) followed by a shoulder at -1500 mV (iii). The reverse scan exhibited a broad peak at -1150 mV (iii) followed by a peak at -700 mV (iv). The multiplicity of anodic peaks may occur due

to (a) dissolution of alloy formed (b) dissolution of the substrate (c) presence and dissolution of more than one type of zinc and (d) dissolution of a metal with different stages of oxidation.
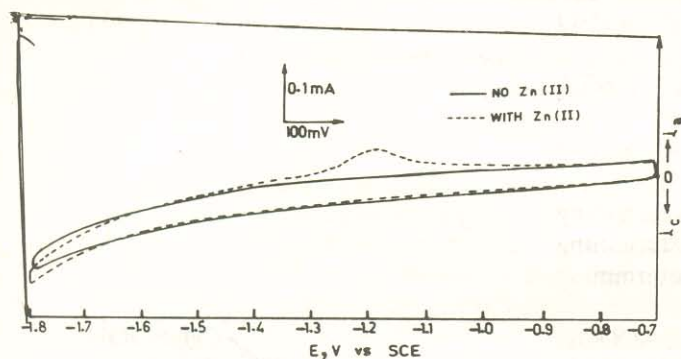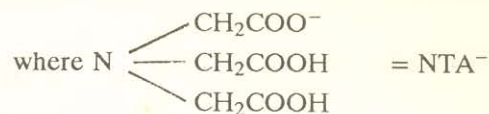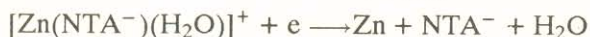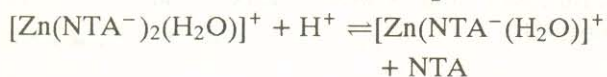

Fig. 2: Typical voltammogram in deoxygenated ZnSO₄ solution containing NTA 5×10^{-3} M at 100 mVs⁻¹ $E_{\lambda,a} = -700$ mV; $E_{\lambda,c} = -1800$ mV

On a glassy carbon substrate 'a' to 'c' may be ruled out. Dissolution of a deposited zinc may take place via monovalent species which is stabilised by complexing anions. At higher potentials the appearance of a peak may be due to the oxidation of monovalent species.

One may visualise the species $[Zn(NTA^-)_2 (H_2O)]^{++}$ undergoing stepwise reduction to zinc [2].

$$[Zn(NTA^-)_2(H_2O)_2]^{++} + e \rightleftharpoons [Zn(NTA^-)_2(H_2O)]^+ + H_2O$$

$$[Zn(NTA^-)_2(H_2O)]^+ + H^+ \rightleftharpoons [Zn(NTA^-(H_2O)]^+ + NTA$$

$$[Zn(NTA^-)(H_2O)]^+ + e \longrightarrow Zn + NTA^- + H_2O$$

where N $\Big\langle$ $\begin{array}{l} CH_2COO^- \\ CH_2COOH \\ CH_2COOH \end{array}$ = NTA⁻
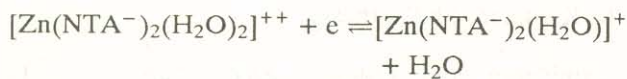
If step 2 is rds,

$$i_c = \vec{K}_c[Zn(NTA^-)_2(H_2O)_2]^{++}[H^+][H_2O]^- \\ \exp - \alpha_c EF/RT$$

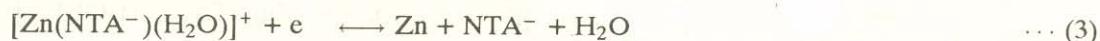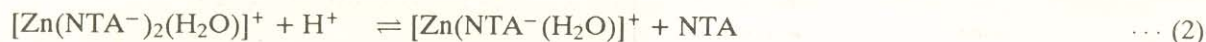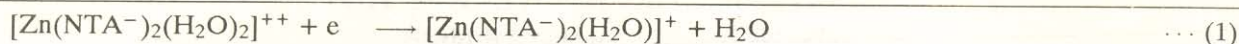The cathodic Tafel slope is 60 mV, and the reaction orders wrt (H⁺) and pH are 1.0 and −1.0.

TABLE–I: Mechanistic parameters obtained for deposition/dissolution of zinc in complex (NTA) bath

No.	Parameters	Experimental value
1.	Anodic Tafel slope	60 ± 10 mV/decade
2.	Cathodic Tafel slope	60 ± 10 mV/decade
3.	Anodic reaction order with respect to divalent zinc complex ions	0.0
4.	Cathodic reaction order with respect to divalent zinc complex ions	+ 0.7
5.	Anodic reaction order with respect to pH	+ 0.33
6.	Cathodic reaction order with respect to pH	+ 0.33
7.	Anodic reaction order with respect to NTA	2 ± 0.2
8.	Cathodic reaction order with respect to NTA	0.0

TABLE–II: Possible schemes for the dissolution and deposition of zinc in baths with zinc complexes

Scheme	Tafel slope Anodic (mV/decade)	Tafel slope Cathodic	Reaction order with respect to Zn(II) complex Anodic	Reaction order with respect to Zn(II) complex Cathodic	Reaction order with respect to NTA Anodic	Reaction order with respect to NTA Cathodic	Reaction order with respect to pH Anodic	Reaction order with respect to pH Cathodic
A	120	40	0.0	+1.0	+1.0	−1.0	−1.0	+1.0
B	60	60	0.0	+1.0	+2.0	0.0	−1.0	+1.0
C	40	120	0.0	+1.0	+2.0	0.0	−2.0	0.0

TABLE–IIa: Possible scheme

$$[Zn(NTA^-)_2(H_2O)_2]^{++} + e \longrightarrow [Zn(NTA^-)_2(H_2O)]^+ + H_2O \qquad \cdots (1)$$

$$[Zn(NTA^-)_2(H_2O)]^+ + H^+ \rightleftharpoons [Zn(NTA^-(H_2O)]^+ + NTA \qquad \cdots (2)$$

$$[Zn(NTA^-)(H_2O)]^+ + e \longleftrightarrow Zn + NTA^- + H_2O \qquad \cdots (3)$$

Scheme A   Step 1   is rate determining
Scheme B   Step 2   is rate determining
Scheme C   Step 3   is rate determining

$$NTA \doteq N \begin{cases} CH_2COOH \\ CH_2COOH \\ CH_2COOH \end{cases} \qquad NTA^- = N \begin{cases} CH_2COOH \\ CH_2COO^- \\ CH_2COOH \end{cases}$$
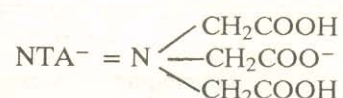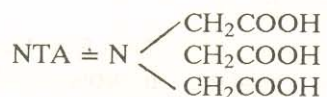
Similarly $i_a = \overleftarrow{K}_a (Zn)(NTA^-)^2(H^+) \exp \alpha aEp/RT$

This suggests an anodic Tafel slope of 60 mV/decade and a reaction order of 2.0 wrt (NTA$^-$) and of -1.0 wrt pH.

Tables I and II present the mechanistic parameters and possible schemes for the dissolution of zinc and zinc deposition from zinc - NTA complexes. Scheme B agrees with the anodic and cathodic reaction orders with respect to NTA. Dependence of reaction orders on pH needs more understanding since the formation and consumption of NTA$^-$ depends upon both NTA and NTA$^-$. The cathodic reaction order with respect to pH is in the same direction. Nonagreement of the anodic reaction order with respect to pH is not easily understandable.

CONCLUSIONS

The deposition of zinc from zinc sulphate solution involves adsorbed intermediates and the first electron transfer is a slow step.

REFERENCES

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2. R M Krishnan, Ph.D., thesis

3. S Srinivasan and Gileadi, *Electrochim Acta*, 11 (1966) 321