

Electrochemical behaviour of zinc acetate complexes: a cyclic voltammetry study

R. Sekar*¹, S. Jayakrishnan¹ and V. S. Muralidharan¹

The search for eco-friendly non-cyanide zinc plating solutions has resulted in the development of zinc acetate baths. Cyclic voltammetric studies of the dissolution and deposition of zinc in the presence of acetate complexes were carried out. In the pH range of 4.5–5.5, zinc acetate complexes underwent successive reduction to zinc. Acetate ions and OH⁻ ions were shown to affect both the dissolution and deposition of zinc. The dissolution of zinc required the participation of OH⁻ ions.

Keywords: Cyclic voltammetry, Dissolution, Electrodeposition, Non-cyanide, zinc acetate, complexes

Introduction

In electrochemistry, the Zn/Zn²⁺ reaction ranks next to the hydrogen and oxygen reduction reactions in importance.¹ Polarographic studies of the uncomplexed zinc ions revealed a reversible two electron transfer process. The development of alternatives to cyanide solutions is an active research area in electroplating, and cyclic voltammetry has been extensively used^{2–4} to study the reduction of non-cyanide complexes. The aim of the present investigation was to further understanding of the deposition and dissolution of zinc in acetate solutions, a widely proposed alternative to cyanide solutions.

Experimental

A glass three electrode cell assembly was used. Glassy carbon, a large platinum foil and a saturated calomel electrode were used as working, counter and reference electrodes respectively. To minimise *IR* drop a finely drawn Luggin capillary positioned very close to the working electrode was used. Potential sweeps were conducted at 5–50 mV s⁻¹ using a potentiostat and the response was recorded on a *x-y* recorder. The solutions were prepared using double distilled water and AnalaR grade chemicals. Experiments were conducted in zinc acetate solutions (0.1 < *x* < 1 M) using potassium acetate (0.1 < *x* < 1 M) as supporting electrolyte. The desired pH of the solutions was maintained by addition of acetic acid.

Results

Figure 1 presents cyclic voltammograms obtained in 0.2 M zinc acetate solution containing 0.1 M potassium acetate at pH 5. When polarised from 0 to -1800 mV, the forward scan exhibited a cathodic peak at -1290 mV. The cathodic peak potentials became more active as sweep rate was increased. When the scan was

reversed an anodic peak appeared at about -900 mV that became more noble with increasing sweep rate. Cathodic peak potentials varied by 160 mV per decade increase in sweep rate.

Figure 2 presents the electrochemical spectra obtained in different acetate ion concentrations at a sweep rate of 10 mV s⁻¹. When polarised from 0 to -1800 mV, the forward scan exhibited a cathodic peak at about -1420 mV that moved to more positive potentials with increasing acetate ion concentration. This suggests that the presence of acetate ions favours the deposition of zinc. When the scan was reversed an anodic peak was observed which occurred at -710 mV in 0.05 M acetate solution and at more positive potentials with increasing acetate ion concentration. Acetate ions hinder the dissolution of deposited zinc, as indicated by the decrease in anodic peak current with increasing acetate concentration.

Figure 3 presents electrochemical data obtained at two zinc ion concentrations at a sweep rate of 10 mV s⁻¹. The forward scan exhibited a cathodic peak at -1280 and -1300 mV respectively in the 0.1 M and 0.2 M zinc solutions. During the reverse scan anodic peaks were observed at -880 and -940 mV respectively. Cathodic peak current increased whereas anodic peak current decreased with increasing zinc ion concentration.

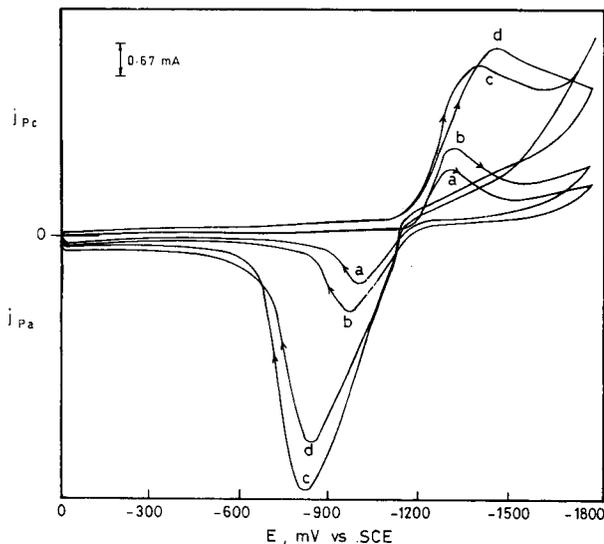
Figure 4 presents cyclic voltammograms obtained in solutions of different pH. When polarised from 0 to -1800 mV, the forward scan exhibited a cathodic peak at -1350 mV at pH 4.5 that became more positive in potential with increasing pH. Cathodic peak current decreased with increasing pH. During the reverse scan an anodic peak was seen at -730 mV at pH 4.5, which moved to more positive potentials with increasing pH. This change suggests that increasing solution pH hindered zinc dissolution. Anodic peak current decreased with increasing pH.

Discussion

Zinc complexes are either square planar or tetrahedral in form. Sterically, square planar complexes are less

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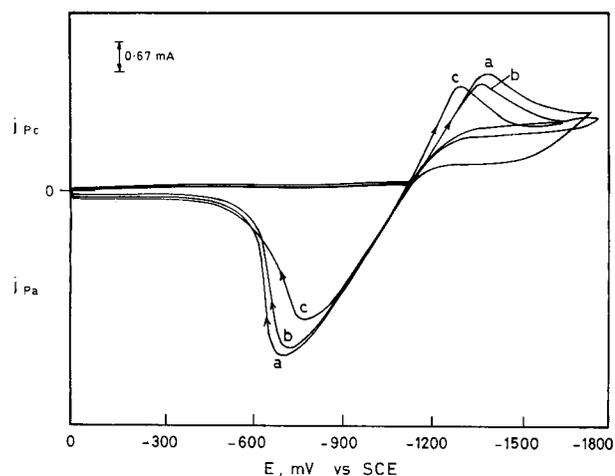


a 5 mV s⁻¹; b 10 mV s⁻¹; c 25 mV s⁻¹; d 50 mV s⁻¹

1 Cyclic voltammogram obtained in 0.2 M (CH₃COO)₂Zn + 0.1 M CH₃COOK solution at given sweep rates

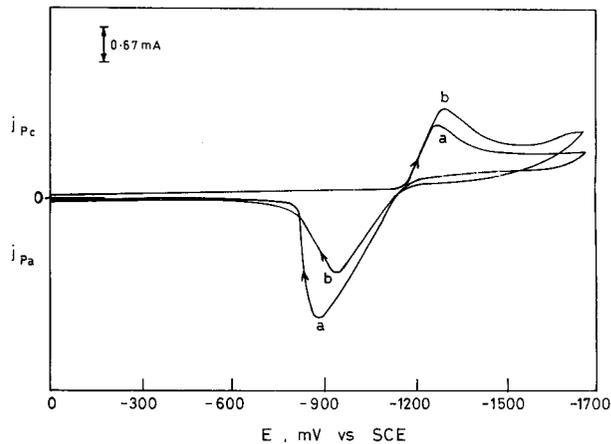
favoured than tetrahedral complexes. The stability of the square planar complexes is favoured by non-bulky ligands characterised by strong polarisation fields. Tetrahedral complexes are favoured by steric requirements relating to simple electrostatic repulsion of charged ligands or to van der Waals repulsion of larger ligands.

Complex shape depends not only on the number of pairs of electrons the central atom possesses but also on how many of these are bond pairs and how many are ion pairs. For example, a complex around an atom with four pairs of electrons may be tetrahedral, trigonal or pyramidal V-shaped if the number of lone pairs is zero, one or two respectively. The substitution of coordinated water molecules by anions (X⁻) affects the cathodic peak potential, since the number of coordinated water molecules determines the discharge potential of the zinc complexes. Substitution of water by X⁻ anions has been shown to result in a tetrahedral structure. Adsorption followed by discharge of the complex is favoured by this structural change.



a 0.05 M CH₃COOK + 0.2 M (CH₃COO)₂Zn; b 0.1 M CH₃COOK + 0.2 M (CH₃COO)₂Zn; c 0.15 M CH₃COOK + 0.2 M (CH₃COO)₂Zn

2 Cyclic voltammogram obtained in given solutions at sweep rate of 10 mV s⁻¹

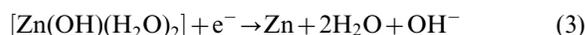
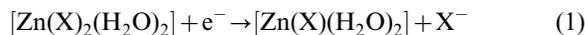


a 0.1 M (CH₃COO)₂Zn + 0.1 M CH₃COOK; b 0.2 M (CH₃COO)₂Zn + 0.1 M CH₃COOK

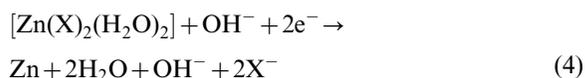
3 Cyclic voltammogram obtained in given solutions at sweep rate of 10 mV s⁻¹

Deposition of zinc

Under transient polarisation conditions in acetate solutions, in the pH range of 4.5–5.5, the deposition of zinc may involve monovalent zinc ions. If the zinc acetate complex is represented as [Zn(X)₂(H₂O)₂] and X⁻ is acetate anion, the reduction may take place as



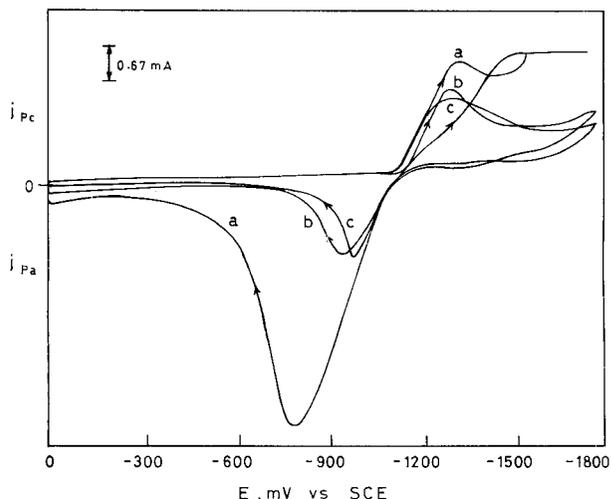
The overall reaction may be represented as



For a slow first electron transfer reaction under Langmuir conditions

$$j_c = K_2 K_1 [Zn(H_2O)_2 (X)_2] \exp - (\alpha_c F \Delta \phi_c / RT) \quad (5)$$

where α_c is the cathodic transfer coefficient, $\Delta \phi_c$ is the



a pH 4.5; b pH 5.0; c pH 5.5

4 Cyclic voltammogram obtained in 0.2 M (CH₃COO)₂Zn + 0.1 M CH₃COOK solutions at given pH values at sweep rate of 10 mV s⁻¹

interfacial electrode potential, and K_2 , K_1 are the rate constants. If the discharge of zinc complex is irreversible^{5,6}

$$E_{p,c} = E^0 + (RT/nF)[\ln(k^0/D)^{1/2} - 0.05\ln(\alpha_c FV/RT) - 0.78] \quad (6)$$

where $E_{p,c}$ is the cathodic peak potential, V is the sweep rate and D is the diffusion coefficient of zinc ions. Plotting $E_{p,c}$ against $\log V$ gives the cathodic Tafel slope. The observed cathodic Tafel slope of 150 ± 10 mV/decade suggests that the first electron transfer is slow

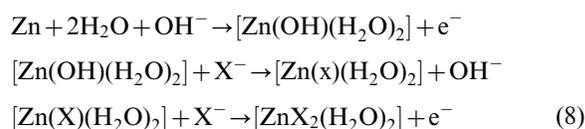
$$j_{p,c} = \left[nF A C_{Zn^{2+}}^0 \sqrt{\pi} D_{Zn^{2+}}^0 (\alpha_c \vartheta / RT) (\varepsilon_i - \varepsilon) \right] \quad (7)$$

where ε_i is the initial potential, $C_{Zn^{2+}}^0$ is the initial concentration of zinc ions, $D_{Zn^{2+}}^0$ is the diffusion coefficient of zinc ions, α_c is the cathodic transfer coefficient, D is the sweep rate and A is the area of the electrode. The slope of a plot of $\log j_{p,c}$ against $\log C_{Zn^{2+}}^0$ gives the reaction order with respect to Zn^{2+} ions. The observed slope of 0.6 confirms this.

Dissolution of zinc

The anodic peak potentials and currents varied with pH and acetate ion concentrations. This suggests that the

dissolution of zinc occurs as



Conclusions

Voltammetric studies revealed that in the pH range of 4.5–5.5, zinc acetate complexes undergo successive reduction to zinc. Acetate ions and OH^- ions affected both the dissolution and deposition of zinc. The dissolution of zinc required the participation of OH^- ions.

References

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