# Role of addition agents in zincate bath – a cyclic voltammetry study

*A. J. Rethinam,*
*G.N.K. Ramesh Bapu and*
*V.S.Muralidharan\**

*Central Electrochemical Research Institute,*
*Karaikudi-630 006, India*

SUMMARY – *To enhance grain homogenisation and brightness various addition agents are employed in zinc plating baths. Triethanolamine, vanillin, dextrin, gelatin and ascorbic acid are added to zincate baths to enhance brightness. Cyclic voltammetric studies were carried out on glassy carbon electrodes from zincate solutions. The deposition of zinc involves a slow second electron transfer. Addition agents shifted the cathodic peak potentials and increased the rate of zinc deposition. Hydrogen evolution was hindered by the addition of triethanolamine and dextrin. The dissolution of zinc was found to be accelerated by these additives.*

**Key words:** Cyclic Voltammetry, Triethanolamine, Vanillin, Dextrin, Gelatine, and Ascorbic acid, Zinc Electroplating.

## INTRODUCTION

Zinc electrodeposits obtained from zincate baths exhibit enhanced grain homogenisation in the presence of additives. Most addition agents adsorb on the electrode surface, blocking the high energy sites for the crystallisation of the metal[1]. In the electrodeposition of metals[2] the formation of a critical micelle concentration is also viewed as important in the mechanism of the action of these compounds. Some compounds may inhibit dendrite growth[3]. Furfuraldehyde[4], thiourea[5] and other substituted aldehydes[6] affect the morphology of zinc deposits.

The present communication deals with cyclic voltammetric studies carried out from zincate solutions containing the organic compounds triethanolamine, vanillin, dextrin, gelatin and ascorbic acid.

## EXPERIMENTAL

All solutions were prepared using AnalaR chemicals and double distilled water. An all glass three electrode cell assembly of 80 cm³ capacity was used for voltammetric studies. Glassy carbon (0.07 cm²), a large platinum foil and a saturated calomel electrode were used as working, counter and reference electrodes respectively. The glassy carbon electrode was polished using 1/0, 2/0, 3/0 and 4/0 emery papers successively, degreased with trichloroethylene, dried and used. To minimise the IR drop a finely drawn capillary was used. The desired potentials between $-1200$ and $-2000$ mV were swept at 5–100 mV s⁻¹ using an Ablab solid state low frequency function generator type LFG1 in conjunction with a Wenking potentiostat Model 70 TSI. A Kipp and Zonen BD 30 X-Y recorder was used to record *E-I* curves. The potentiostat output was read using a digital multimeter type HIL Model 2141. Experiments were carried out at 30°C in zincate solutions containing 0.12 M zinc oxide, 2.75 M sodium hydroxide and various concentrations of organic compounds such as triethanolamine (0.30 M), vanillin (0.013 M), dextrin (2 g dm⁻³), gelatin (2 g dm⁻³) and ascorbic acid (0.011 M). The experiments were repeated to confirm reproducibility.

## RESULTS

Table 1 presents the details of the addition agents used. These compounds are brighteners when used alone or in combination in zinc plating. The results on the influence of these compounds on the dissolution and deposition of zinc in zincate solutions are as follows:

### Zincate solutions

When polarised from $-1200$ to $-2000$ mV (SCE) in zincate solutions containing 0.12 M zinc oxide and 2.75 M sodium hydroxide, the forward scan exhibited a current rise at $-1585$ mV at 5 mV s⁻¹ (Figure1). An increase in current was observed beyond $-1750$ mV due to hydrogen evolution. When the scan was reversed, the zero current crossing potential (ZCCP) occurred at *ca.*$-1585$ mV. A sharp anodic peak appeared at $-1440$ mV. The cathodic peak potentials increased with sweep rates. They varied $50\pm10$ mV per decade change of sweep rate.

### Effect of additives
*(i) Triethanolamine (TEA)*
Introduction of 0.30 M triethanolamine in zincate solutions did not affect the electrochemical spectrum (Figure 2). When

**Table I.  Details of the addition agents used**

| Compound | Molecular weight | Formula |
|---|---|---|
| Triethanolamine | 149.19 | $C_6H_{15}NO_3$ |
| Vanillin | 152.15 | $CH_3OC_6H_3(OH)CHO$ |
| Dextrin | Polymer | $(C_8H_{10}O_5)_n.xH_2O$ |
| Ascorbic Acid | 176.13 | $C_6H_8O_6$ |
| Gelatin | ——— | Natural product |

**Table II. Parameters derived for the deposition of zinc from cyclic voltammograms at 5 mV s⁻¹.**

| System | Discharge potential /mV vs SCE | $E_{p.c}$ /mV vs SCE | $I_{p.c}$/mA |
|---|---|---|---|
| Zincate solution (0.12 M zinc oxide + 2.75 M sodium hydroxide) | –1585 | –1580 | 0.56 |
| Zincate solution + 0.30 M triethanolamine | –1650 | –1660 | 0.80 |
| Zincate solution + 0.30 M triethanolamine + 0.013M vanillin | –1650 | –1710 | 0.92 |
| Zincate solution + 0.30 M triethanolamine + 2 g dm⁻³ dextrin | –1650 | –1690 | 0.86 |
| Zincate solution + 0.30 M triethanolamine + 2 g dm⁻³ gelatin | –1650 | –1700 | 1.32 |
| Zincate solution + 0.30 M triethanolamine + 0.011 M ascorbic acid | –1650 | –1750 | 0.99 |
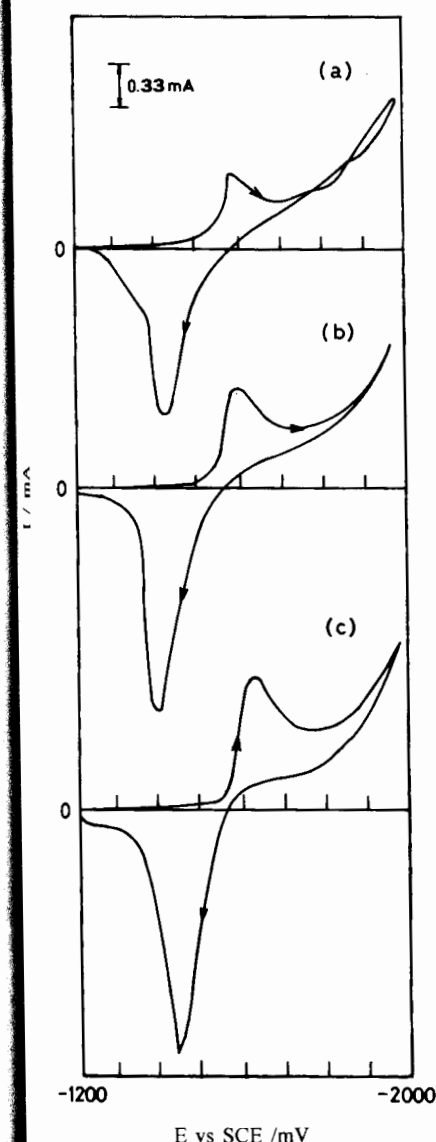


*Figure 1. Cyclic voltammograms obtained in 0.12 M zinc oxide + 2.75 M sodium hydroxide solutions at different sweep rates. a) 5 mV s⁻¹ b) 10 mV s⁻¹ c) 20 mV s⁻¹*
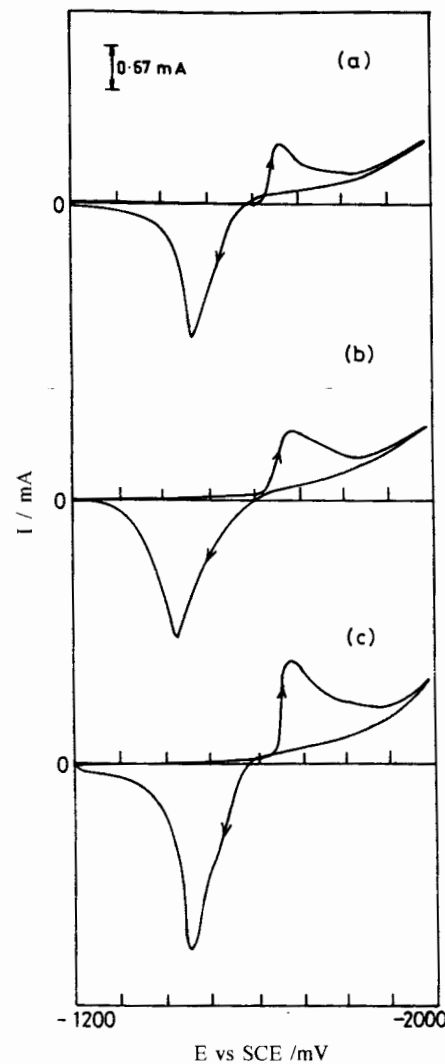


*Figure 2. Cyclic voltammograms obtained in 0.12 M zinc oxide + 2.75 M sodium hydroxide solutions containing 0.30 M triethanolamine at different sweep rates. a) 5 mV s⁻¹ b)10 mVs⁻¹ c)20 mVs⁻¹*

polarised from –1200 to –2000 mV, the current started rising beyond –1600 mV. A well-defined cathodic peak appeared at –1660 mV. When the scan rate was 50 mV s⁻¹, (data not shown), hydrogen evolution was found to occur beyond –1800 mV. During the reverse scan, an anodic peak appeared at –1480 mV. It can be seen from Figure 2 that the cathodic peak potentials and currents did not vary significantly with sweep rate.

*(ii) Vanillin*
Figure 3 presents the electrochemical data obtained in the presence of 0.30 M triethanolamine and 0.013 M vanillin. When polarised from –1200 to –2000 mV, the forward scan exhibited a current rise beyond –1650 mV and a cathodic peak potential at –1710 mV. On reversing the scan, the zero current crossing potential (ZCCP) appeared at –1600 mV followed by an anodic peak at –1470 mV. The cathodic peak potentials increased with sweep rates.

*(iii) Dextrin*
The voltammetric spectrum obtained in the presence of the 0.30 M triethanolamine and 2 g dm⁻³ dextrin containing zincate bath is shown in Figure 4. When polarised from –1200 to –2000mV, the forward scan exhibited a cathodic peak at –1690 mV. A sharp current rise beyond –1800 mV was attributed due to hydrogen evolution. On reversing the scan the ZCCP occurred at –1550 mV. An anodic peak was noticed at –1430 mV. Cathodic peak potentials increased with sweep rates.

*(iv) Gelatin*
Figure 5 presents the cyclic voltammogram obtained in the presence of 2 g dm⁻³ gelatin and 0.30 M triethanolamine. During the forward scan the current started increasing beyond –1650mV with a cathodic peak at –1700 mV. Cathodic peak potentials did not vary significantly with sweep rate. On reversing the scan, the ZCCP occurred at –1600 mV followed by an anodic peak at –1480 mV.

*(v) Ascorbic acid*
When polarised from –1200 to –2000 mV, the electrochemical spectrum obtained in the presence of 0.30 M triethanolamine and 0.011 M ascorbic acid exhibited a cathodic peak at –1750 mV (Figure 6). On reversing the scan, the ZCCP appeared at –1600 mV and an anodic peak was observed at –1500 mV. The cathodic peak potentials increased with sweep rates.

## DISCUSSION

### Deposition of Zinc
Of fundamental importance for establishing the mechanism of cathodic reduction of Zinc (II) are the composition and structure of the complex ions that form in electrolytes. The composition of zinc complexes has been reported earlier[7]. In solutions of high alkali concentration, the formation of a tetrahydroxy zincate ion was revealed by measurements of equilibrium potentials[8], vibrational spectroscopy[9] and NMR spectroscopy[10]. In
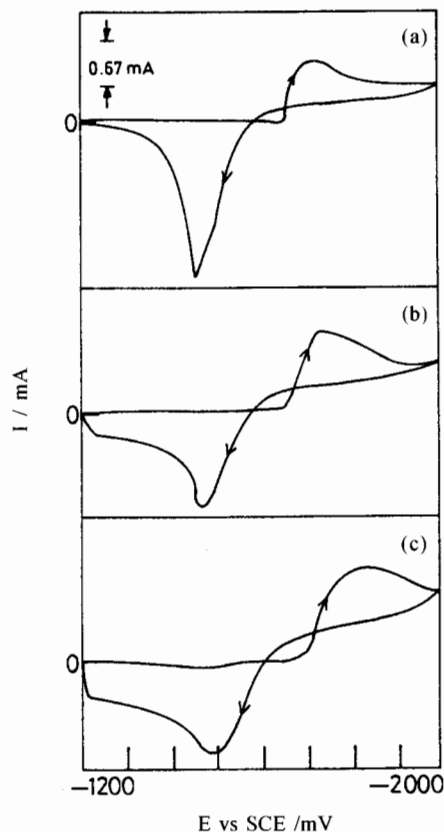
Figure 3. Cyclic voltammograms obtained in 0.12 M zinc oxide + 2.75 M sodium hydroxide solutions containing 0.30 M triethanolamine and 0.013 M vanillin at different sweep rates.
a) 5 mV s$^{-1}$ b)10 mV s$^{-1}$ c)20 mV s$^{-1}$
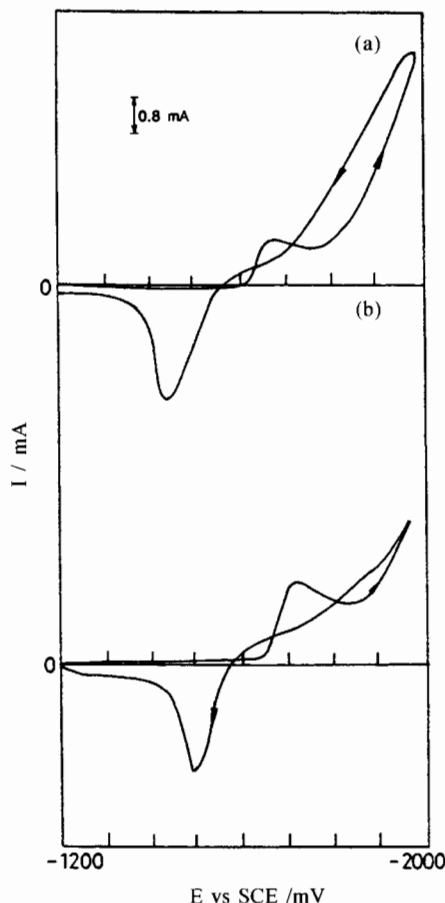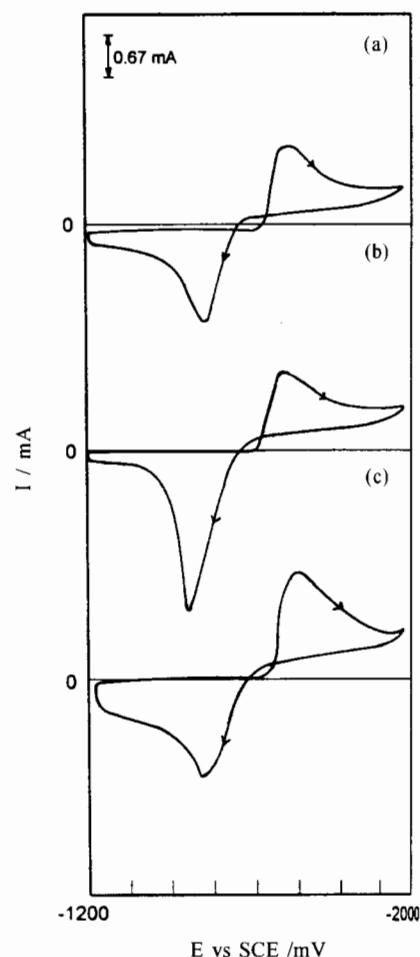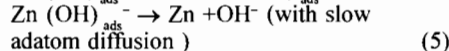

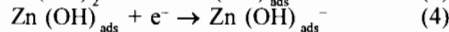
Figure 4. Cyclic voltammograms obtained in 0.12 M zinc oxide + 2.75 M sodium hydroxide solutions containing 0.30 M triethanolamine and 2 g dm$^{-3}$ dextrin at different sweep rates.
a) 5 mV s$^{-1}$ b)20 mV s$^{-1}$
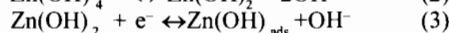


Figure 5. Cyclic voltammograms obtained in 0.12 M zinc oxide + 2.75 M sodium hydroxide solutions containing 0.30 M triethanolamine and 2 g dm$^{-3}$ gelatin at different sweep rates.
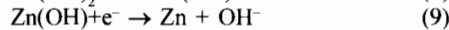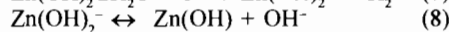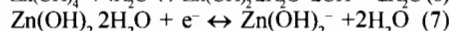a) 5 mV s$^{-1}$ b)10 mV s$^{-1}$ c)20 mV s$^{-1}$

the presence of low concentrations of ligands, the solubility method[11] revealed Zn (II) hydroxy complexes with a smaller number of hydroxy groups, specifically $Zn(OH)$, $Zn(OH)_2$ and $Zn(OH)_3^-$. On amalgamated Zinc, the reduction of Zn (II) species was

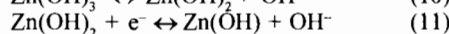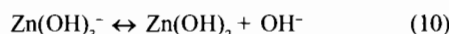$$Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^- \qquad (1)$$
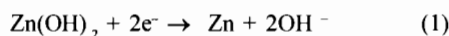
where the charge is transferred to a neutral species within a step[12]. The act of two or more electron transfers in a single step is less probable on a solid electrode[13], and hence the following sequence was suggested,

$$Zn(OH)_4^{2-} \leftrightarrow Zn(OH)_2 + 2OH^- \qquad (2)$$
$$Zn(OH)_2 + e^- \leftrightarrow Zn(OH)_{ads} + OH^- \qquad (3)$$
$$Zn(OH)_{ads} + e^- \rightarrow Zn(OH)_{ads}^- \qquad (4)$$
$$Zn(OH)_{ads}^- \rightarrow Zn + OH^- \text{ (with slow}$$
$$\text{adatom diffusion )} \qquad (5)$$

or if hydration is allowed for[14,15],

$$Zn(OH)_4^{2-} \cdot 4H_2O \leftrightarrow Zn(OH)_2 2H_2O + 2OH^- + 2H_2O (6)$$
$$Zn(OH)_2 2H_2O + e^- \leftrightarrow Zn(OH)_2^- + 2H_2O \quad (7)$$
$$Zn(OH)_2^- \leftrightarrow Zn(OH) + OH^- \qquad (8)$$
$$Zn(OH) + e^- \rightarrow Zn + OH^- \qquad (9)$$

If the $Zn(OH)_3^-$ ion dominates in the solution the electrode process is[16],

$$Zn(OH)_3^- \leftrightarrow Zn(OH)_2 + OH^- \qquad (10)$$
$$Zn(OH)_2 + e^- \leftrightarrow Zn(OH) + OH^- \qquad (11)$$

$$Zn(OH) + e^- \leftrightarrow Zn + OH^- \qquad (9)$$

In the above cases, the electroactive species are $Zn(OH)_2$ and $Zn(OH)_{ads}$. A four step mechanism which involves the attachment of the first electron to $Zn(OH)_3^-$ was also reported earlier[17]. The quantum mechanical theory emphasizes that despite the predominance of high co-ordinated hydroxy complexes of Zn(II) electrolyte their discharge is preceded by a ligand abstraction stage with the formation of neutral species $Zn(OH)_2$. This stage occurs at the electrode surface and is characterised by an endothermic effect, which is a constituent of the activation energy for the entire electroreduction process[17].

In the present study, under transient polarisation conditions the deposition of zinc may occur as,

$$Zn(OH)_4^{2-} \leftrightarrow Zn(OH)_3^- + OH^- \qquad (12)$$
$$Zn(OH)_3^- \leftrightarrow Zn(OH)_2 + OH^- \qquad (13)$$
$$Zn(OH)_2^- \leftrightarrow ZnOH + OH^- \qquad (14)$$
$$ZnOH + e^- \rightarrow Zn + OH^- \text{ (slow)} \qquad (9)$$
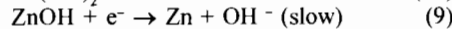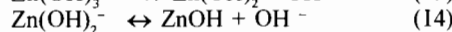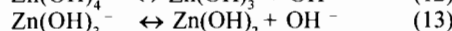
so that for the slow step classical theory[13] gives

$$i_c = \vec{k_4} k_3 k_2 k_1 [Zn(OH)_4]^{2-} [OH^-]^{-3} exp^{(1-\beta) F \Delta\phi / RT} (15)$$

where $k_1$, $k_2$ and $k_3$ are the equilibrium rate constants for the above reactions (12) to (14) and $\vec{k_4}$ is the forward rate constant for the slow step.

As there was a large potential separation between anodic and cathodic peaks, one could write[18,19]

$$E_{p.c} = E^\circ + RT/nF \, [lnk_0/\sqrt{D} - 0.5 \, ln$$
$$(-\alpha_c Fv/RT) - 0.78] \qquad (16)$$

where $E_{p.c}$ is the cathodic peak potential, $v$ is the sweep rate, $D$ is the diffusion coefficient of zinc ions. The plot of $E_{p.c}$ vs log $v$ would give a value of $(2.303RT/-\alpha_c F)$ and the observed value of $54\pm9$ mV/decade. This is in agreement with the experimental results obtained for sweep rates 5–100 mV s$^{-1}$ (Figure 7).

The addition agents did not affect the discharge potential of zinc deposition (Table II). However they shifted the cathodic peak potentials and increased the rate of zinc deposition. The cathodic peak current was found to be greater in the presence of triethanolamine and gelatin. In general, in the presence of triethanolamine all the addition agents employed in this study enhanced zinc deposition, perhaps by adsorbing only on the grown zinc nuclei and so promoting the nucleation of zinc on the entire glassy carbon surface.
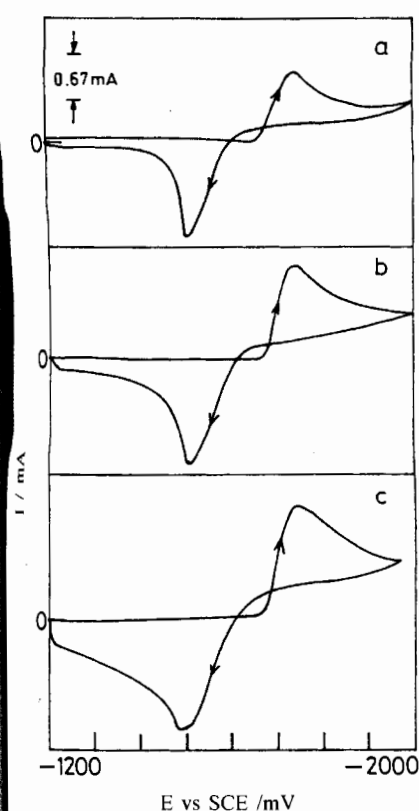
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Figure 6. Cyclic voltammograms obtained in
0.12 M zinc oxide + 2.75 M sodium
hydroxide solutions containing 0.30 M
triethanolamine and 0.011 M ascorbic acid at
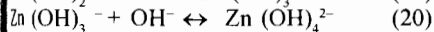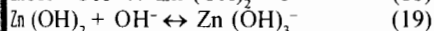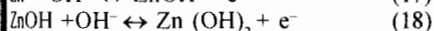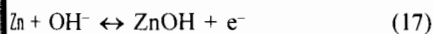different sweep rates.
a) 5 mV s⁻¹ b)10 mV s⁻¹ c)20 mV s⁻¹



Figure 7. Variation of cathodic peak potentials with log sweep rate.
□–□–□–□ No additive;
o-o-o-o 0.30 M triethanolamine
Δ–Δ–Δ–Δ– 0.30 M triethanolamine + 0.013 M vanillin;
∇–∇–∇–∇– 0.30 M triethanolamine + 2g dm⁻³ dextrin;
◇–◇–◇–◇– 0.30 M triethanolamine + 2g dm⁻³ gelatin;
++++ 0.30 M triethanolamine + 0.011 M ascorbic acid;

## Hydrogen Evolution

E-log $i_c$ curves were obtained at the sweep rate of 5 mV s⁻¹ in the potential range of -1750 to -2000mV (Figure 8). Addition of triethanolamine decreased the rate of hydrogen evolution. In the presence of dextrin, triethanolamine increased the rate of hydrogen evolution.

## Dissolution of Zinc

Under transient polarisation conditions, the dissolution of zinc may occur according to,

$$Zn + OH^- \leftrightarrow ZnOH + e^- \tag{17}$$
$$ZnOH + OH^- \leftrightarrow Zn(OH)_2 + e^- \tag{18}$$
$$Zn(OH)_2 + OH^- \leftrightarrow Zn(OH)_3^- \tag{19}$$
$$Zn(OH)_3^- + OH^- \leftrightarrow Zn(OH)_4^{2-} \tag{20}$$

The zero current crossing potential (ZCCP) that appears in reversing the scan, is the corrosion potential of deposited zinc in that medium. ZCCPs of –1600 mV were observed in the presence of triethanolamine containing additives suggesting that the medium favours the corrosion of zinc (Table III).

Anodic peak potentials and anodic peak currents increased in the presence of additives suggesting they favoured dissolution of zinc.

## CONCLUSIONS

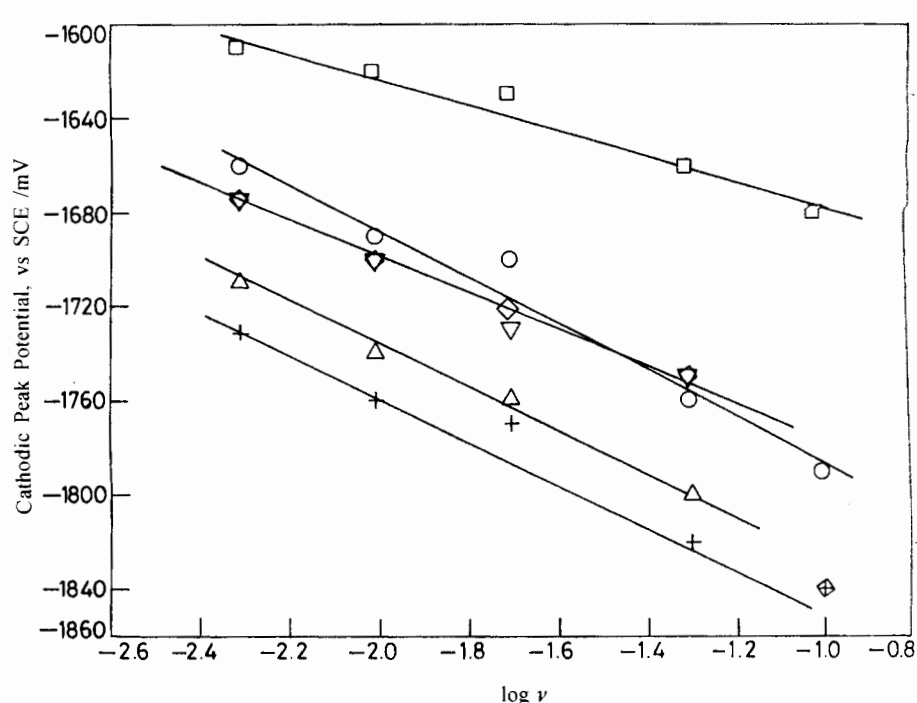Voltammetric studies carried out on glassy carbon from zincate solutions revealed that zincate undergoes successive electroreduction to zinc. The second electron transfer is slow. Addition agents shifted the cathodic peak potentials and increased the rate of zinc deposition. In presence of triethanolamine, they enhanced zinc deposition. Hydrogen evolution was hindered by the addition of triethanolamine and dextrin. The dissolution of zinc was found to be accelerated by these additives.
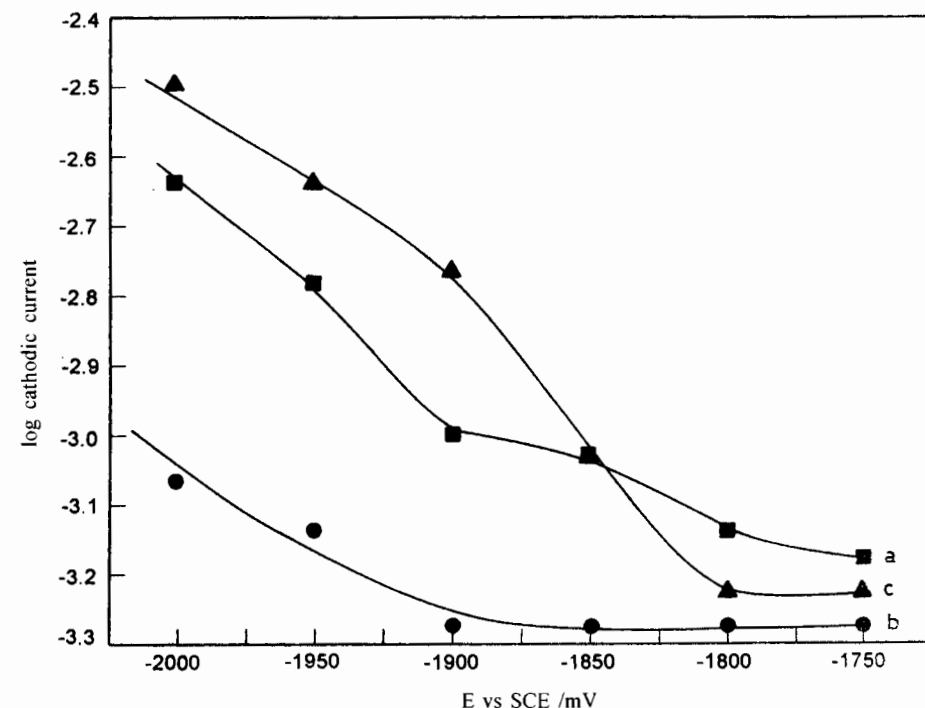
Figure 8. E-logi$_c$ curves for hydrogen evolution at 5 mV s⁻¹
■–■–■–■ No additive;
•–•–•–• 0.30 M triethanolamine
▲–▲– ▲–▲– 0.30 M triethanolamine + 2 g dm⁻³ dextrin

**Table III. Parameters derived for the dissolution of zinc from cyclic voltammograms at 5 mV s$^{-1}$.**

| System | ZCCP vs SCE /mV | $E_{p,a}$ vs SCE /mV | $I_{p,a}$/mA |
|---|---|---|---|
| Zincate solution (0.12 M zinc oxide + 2.75 M sodium hydroxide) | −1585 | −1440 | 1.32 |
| Zincate solution + 0.30 M triethanolamine | −1580 | −1480 | 1.99 |
| Zincate solution + 0.30 M triethanolamine + 0.013M vanillin | −1600 | −1470 | 2.44 |
| Zincate solution + 0.30 M triethanolamine + 2 g dm$^{-3}$ dextrin | −1600 | −1430 | 2.0 |
| Zincate solution + 0.30 M triethanolamine + 2 g dm$^{-3}$ gelatin | −1600 | −1480 | 1.65 |
| Zincate solution + 0.30 M triethanolamine + 0.011 M ascorbic acid | −1600 | −1500 | 1.58 |

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