

Role of triethanolamine and furfuraldehyde on the electrochemical deposition and dissolution behaviour of zinc

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The search for the development of non-cyanide zinc plating baths resulted in identification of newer complexing ligands. The deposition and dissolution of zinc was studied by cyclic voltammetric studies using a bath composition consisted of 0.12M Zinc oxide, 2.75M sodium hydroxide and required quantity of triethanolamine and furfuraldehyde. Glassy carbon (GC), Platinum and SCE were used as working electrode, counter electrode and reference electrode respectively. The studies were made at different concentrations of the above additives at various scan rates at 30°C. The pH of the bath was maintained at 11.5 to 12.0. The deposition of zinc from zincate solutions undergoes successive reduction to zinc. The chemical step followed by first electron transfer is the slow step. Triethanolamine and furfuraldehyde were found to participate in the electron transfer process. Detailed mechanism of deposition and dissolution in presence of triethanolamine and furfuraldehyde are discussed.

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Organic compounds are added to plating baths to increase polarization even at relatively low current densities. They improve the quality of the deposit in terms of adherence, size and grain homogenization. They may also inhibit the formation of dendrites and whiskers¹. The organic compounds affect nucleation and crystallization of the electrodeposit. Formation of critical micelle concentration by the organic compounds affects the electro deposition of metals². Developments in zinc plating was reviewed recently³. In alkaline non-cyanide systems, newer compositions offer deposits with brightness, adhesion and ductility comparable to that obtained from cyanide baths⁴. An amorphous deep black powdery deposit over almost the entire acceptable range of operating conditions was obtained from a solution of ZnO and NaOH⁵. Earlier work in developing a substitute for cyanide centered on the use of chelating or complexing agents such as gluconate and borogluconate⁶.

Cyclic voltammetry was employed to study the electrochemical behaviour of non-cyanide zinc complex⁷. Voltammetric studies carried out on platinum from zinc ethanolamine complexes in pH 5.0 using 0.02M sodium

sulphate as supporting electrolyte revealed that the complex underwent successive reduction to zinc with the formation of mono valent zinc⁸. Formaldehyde, benzaldehyde, furfuraldehyde and thiourea hindered the deposition and dissolution of zinc⁹⁻¹¹. The present communication reports the investigation on the role of triethanolamine and furfuraldehyde on the deposition and dissolution of zinc from zincate solutions.

Experimental Procedure

All solutions were prepared by using analar grade chemicals and double distilled water. An all glass, three-electrode cell assembly of 80 mL capacity was used for the voltammetric studies. A glassy carbon (0.07 cm²), a large platinum foil and saturated calomel electrode were used as working, counter and reference electrodes respectively. The glassy carbon electrodes were polished mechanically using 1/0, 2/0, 3/0 and 4/0 emery papers successively, degreased with trichloroethylene and used. It was kept very close to the working electrode surface to minimise IR drop. The desired potentials were swept (5-100 mV/s) using a potentiostat and the response was recorded on X-Y recorder. Experiments were carried out at 30°C in zinc oxide (0.12M), sodium hydroxide (2.75M)

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along with triethanolamine ($0.075 < x < 0.3\text{M}$) and or furfuraldehyde ($0.012 < x < 0.048\text{M}$). The experiments were repeated to ensure reproducibility.

Results

Cyclic voltammetry studies

Zincate solutions

When polarized from -1200 to -2000 mV, the forward scan exhibited a cathodic peak at -1562 mV at 56 mV/s (Fig. 1). Beyond -1750 mV, current increased due to hydrogen evolution. When the scan was reversed, the zero current crossing potential (ZCCP) occurred at -1550 mV. A sharp anodic peak appeared at -1440 mV at a scan rate of 5 mV/s. The cathodic peak was found to shift towards more negative potentials (Table 1) with sweep rates. They varied 80 ± 10 mV/decade change of sweep rate. Anodic peak potentials varied within ± 50 mV with the decade change in sweep rate.

Effect of triethanol amine (TEA) addition

Introduction of triethanol amine in zincate solutions did not alter the electrochemical spectrum (Fig. 2). When polarised from -1200 to -2000 mV, current started rising beyond -1600 mV. A cathodic peak appeared at -1680 mV in the solution containing 0.075 mM TEA. Hydrogen evolution was found to occur beyond -1800 mV. During the reverse scan an anodic peak appeared beyond -1450 mV.

When the triethanol amine concentration was varied, the cathodic peak potentials became active while peak current decreased (Table 2). Anodic peak current varied significantly while potentials were not affected by TEA concentration.

Table 1—Effect of sweep rate on the deposition of zinc from 0.12 M ZnO + 2.75M NaOH solutions

Sweep rate (mV/s)	$E_{p,c}$ (mV Vs SCE)	$i_{p,c}$ (mA)
5	-1562	0.938
10	-1576	1.206
50	-1640	2.278
100	-1675	3.015

Table 2—Effect of triethanolamine concentration on the deposition of zinc at 50 mV/s sweep rate

Concentration (mM)	$E_{p,c}$ (mV Vs SCE)	$i_{p,c}$ (mA)
0	-1640	2.278
0.075	-1680	2.221
0.150	-1660	1.876
0.225	-1720	1.541
0.300	-1700	2.010

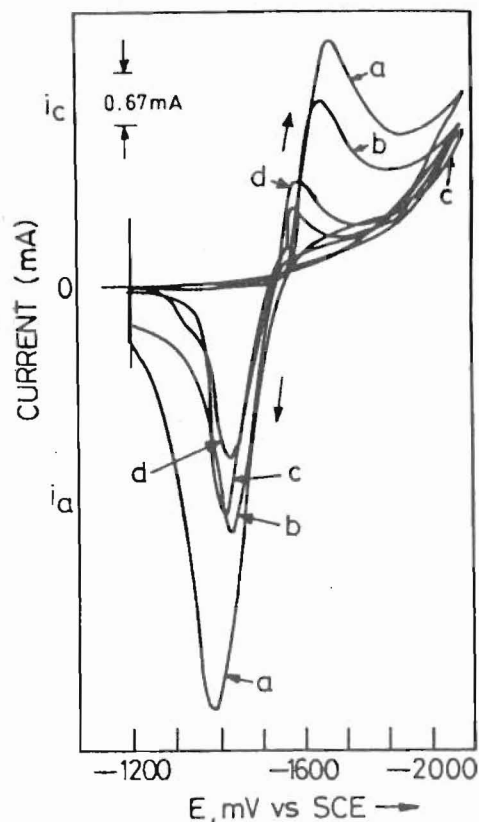


Fig. 1—Cyclic voltammograms in $(0.12\text{M ZnO} + 2.75\text{M NaOH})$ at various sweep rates. (a) 5 mV/s, (b) 10 mV/s, (c) 50 mV/s, (d) 100 mV/s

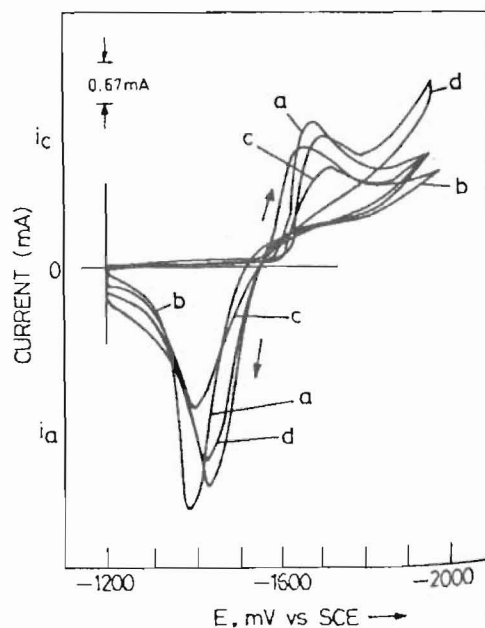


Fig. 2—Cyclic voltammograms in $(0.12\text{M ZnO} + 2.75\text{M NaOH})$ containing various concentrations of triethanol amine at 50 mV/s sweep rate. (a) 0.075 mM, (b) 0.150 mM, (c) 0.225 mM, (d) 0.300 mM

Effect of furfuraldehyde addition

Furfuraldehyde (0.012 mM) was added to zincate solutions and when polarised from -1200 to -2000 mV, the forward scan exhibited a current rise beyond -1550 mV. A cathodic peak appeared at -1630 mV (Fig. 3). Hydrogen evolution was found to start around -1750 mV. When the scan was reversed an anodic peak appeared around -1400±20 mV. Increase of furfuraldehyde concentration did not vary cathodic peak potentials significantly, but it changes the peak current (Table 3).

Effect of triethanolamine and furfuraldehyde addition

In presence of 0.15 mM TEA, various amounts of furfuraldehyde were added to zincate solutions. Figure 4 presents the electrochemical spectrum obtained in zincate solutions containing 0.15 mM TEA and various amounts of furfuraldehyde. The forward scan exhibited a cathodic peak at -1740 mV (curve a of Fig. 4). Hydrogen evolution was found to occur beyond -1780 mV. Though TEA and furfuraldehyde additions shifted the $E_{p,c}$ from -1660 to -1740 mV, the variations in concentrations of furfuraldehyde did not change $E_{p,c}$ (Table 4). However, cathodic peak currents increased slightly with furfuraldehyde concentrations.

Discussions

Mechanism of zinc deposition from zincate solutions

In an electrochemical reduction of complex species as is that of Zn(II) present in alkaline zincate solutions, the overall reaction changes its stoichiometry with changing concentration of the ligand. Thus, in dilute alkali solutions¹² the following reaction occurs,

Table 3—Effect of furfuraldehyde concentration on the deposition of zinc at 50 mV/s sweep rate

Concentration (mM)	$E_{p,c}$ (mV Vs SCE)	$i_{p,c}$ (mA)
0	-1640	2.278
0.012	-1630	2.010
0.024	-1680	2.814
0.036	-1690	2.680
0.048	-1650	3.140

Table 4—Effect of furfuraldehyde concentration in presence of 0.15m M TEA on the deposition of zinc at 50 mV/s sweep rate

Concentration (mM)	$E_{p,c}$ (mV Vs SCE)	$i_{p,c}$ (mA)
0	-1660	1.876
0.012	-1740	1.608
0.024	-1740	1.809
0.036	-1740	1.675
0.048	-1740	1.608

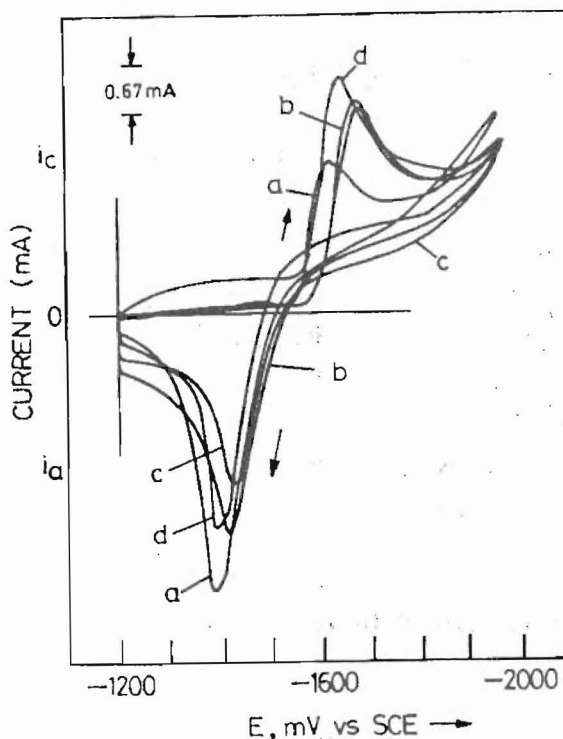


Fig.3—Cyclic voltammograms in (0.12M ZnO + 2.75M NaOH) containing various concentrations of furfuraldehyde at 50mV/s sweep rate.
(a) 0.012 mM, (b) 0.024 mM, (c) 0.036 mM, (d) 0.048 mM.

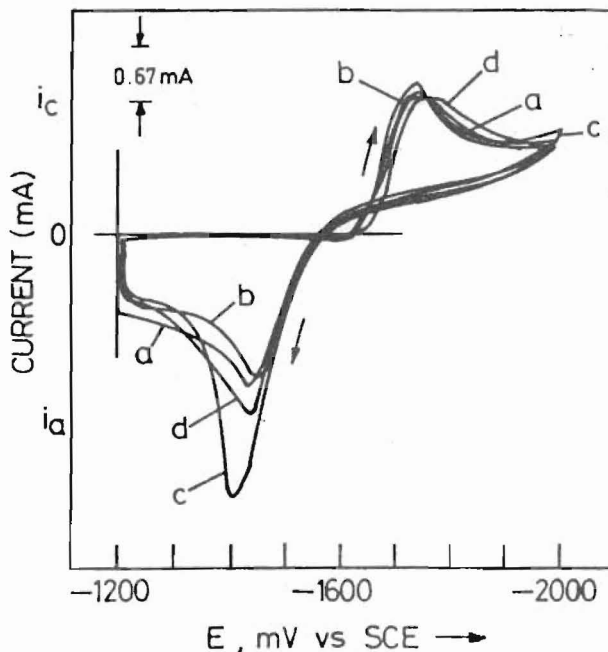
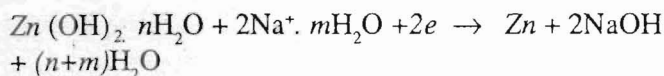
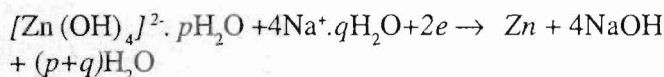


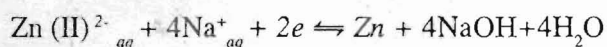
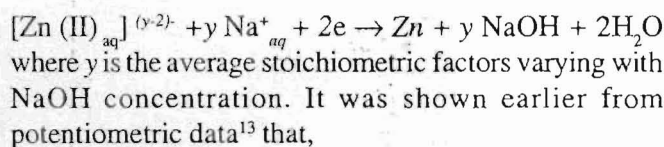
Fig.4—Cyclic voltammograms in (0.12M ZnO + 2.75M NaOH) and 0.15 mM triethanolamine with various concentrations of furfuraldehyde at 50 mV/s sweep rate.
(a) 0.012 mM, (b) 0.024 mM, (c) 0.036 mM, (d) 0.048 mM



While at high hydroxide concentrations the reaction may be,



Or in general,



On this basis it was assumed that $[\text{Zn}(\text{II})]^{2-}$ in the tetrahydro complex seems to be stable at the highest NaOH concentrations attainable i.e. it appeared not to exhibit any acidity. In the pH range 1 to 7M NaOH

solutions, zinc exists as $[\text{Zn}(\text{OH})_4]^{2-}$ as revealed from IR and Raman spectra^{14,15}. In another study, it was shown that $\text{Zn}(\text{OH})_2$ is the electroactive species in NaOH solutions of <3M concentration¹⁶. Anodic

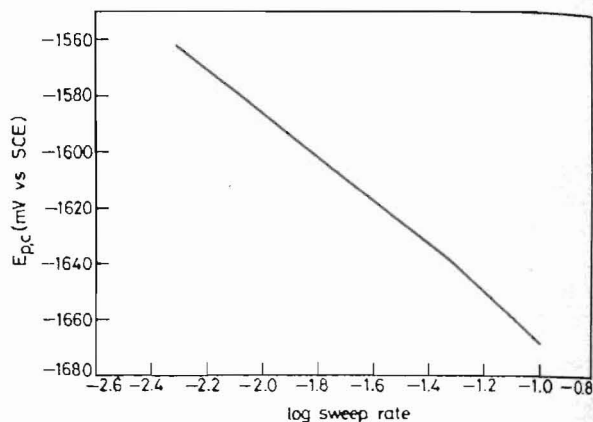


Fig.5—Variation of cathodic peak potential $E_{p,c}$ with log sweep rate in (0.12M ZnO + 2.75M NaOH)

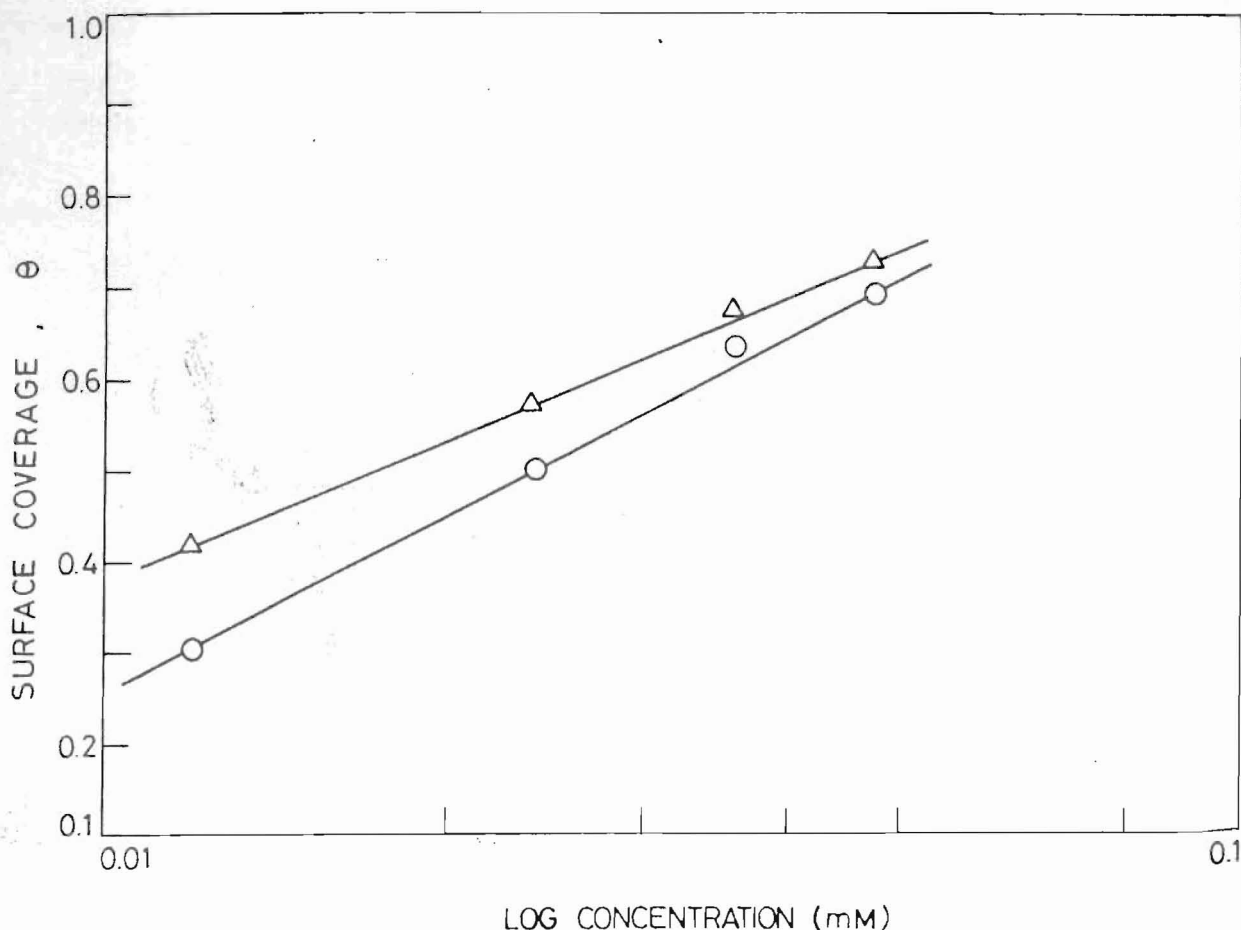
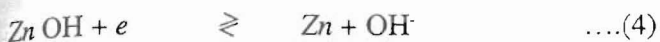
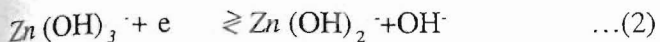
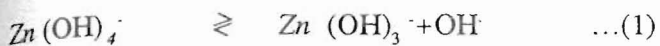


Fig.6—Surface coverage θ versus log concentration of triethanol amine at various sweep rates.
O-O-O 50 mV/s; Δ - Δ - Δ 100 mV/s.

dissolution of zinc amalgams revealed that $Zn(OH)^+$ was the electroactive species¹⁷. On solid electrode, $[Zn(OH)_3]$ was found to be the electroactive species¹⁸.

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



For the slow step (3),

$$i_c \rightarrow i_c = k_3 k_2 k_1 [(ZnOH)_4^{2-}] (OH^-)^2 \exp(-F\Delta\phi/RT)$$

where k_3, k_2, k_1 are the rate constants; $\Delta\phi$ is the interfacial potential difference. As there was a large potential separation between anodic and cathodic peaks, one would write^{19,20},

$$E_{p,c} = E^\circ + RT/nF [\ln k^\circ / \sqrt{D} - 0.5 \ln \alpha_c / RT - 0.78] \quad \dots(5)$$

where $E_{p,c}$ is the cathodic peak potential, v is the sweep rate, D is the diffusion coefficient and α_c is the transfer coefficient.

The plot of $E_{p,c}$ versus $\log v$ would give a cathodic tafel slope. Fig. 5 presents the variation of $E_{p,c}$ with \log sweep rates. The observed values of 80 mV/decade confirms the chemical step followed by first electron step, $Zn(OH)_2^- \rightarrow ZnOH + OH^-$, as slow.

TEA adsorbs on the electrode surface due to the interaction of lone pair of electrons on nitrogen atom. The extent of adsorption and decrease of cathodic peak current depends on the electron density on nitrogen.

Surface coverage due to TEA may be obtained as

$$\theta = (i_{p,c}^1 - i_{p,c}) / i_{p,c}$$

where $i_{p,c}^1$ and $i_{p,c}$ are the cathodic peak currents in absence and presence of TEA. Surface coverage θ varied with TEA concentration (Fig. 6) and Temkin adsorption isotherm was found to be obeyed.

Hydrogen evolution reaction

Figs 7 and 8 present the E - $\log i_c$ curves obtained at 10 mV/sec for hydrogen evolution reaction. Presence of TEA and furfuraldehyde in zincate solutions hindered hydrogen evolution. They offer inhibition by adsorbing on the electrode surface. The inhibition was found to increase with TEA and furfuraldehyde concentrations.

Conclusion

Voltammetric studies carried out on glassy carbon

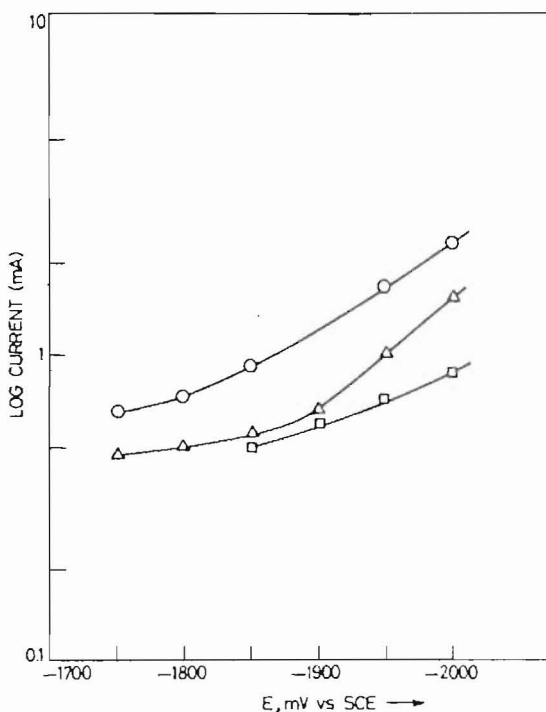


Fig.7—Effect of triethanol amine concentration on hydrogen evolution reaction (E - $\log i_c$) O-O-O No triethanolamine Δ-Δ-Δ 0.15 mM Triethanolamine. □-□-□ 0.225 mM triethanolamine.

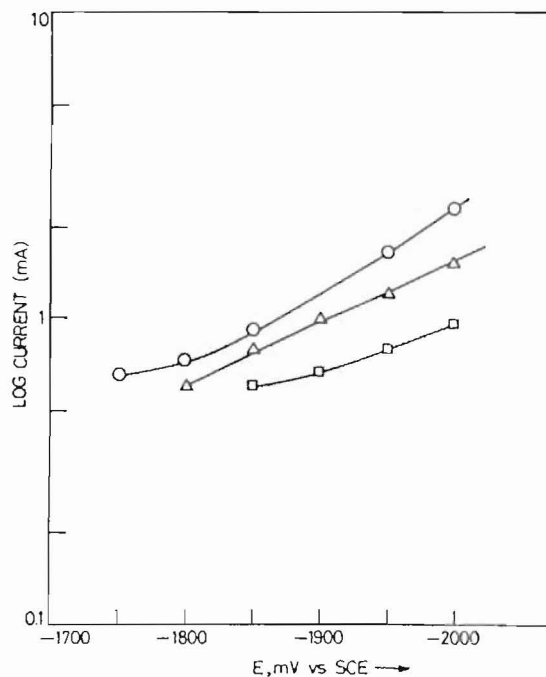


Fig.8—Effect of furfuraldehyde concentration on hydrogen evolution reaction (E - $\log i_c$). O-O-O No furfuraldehyde. Δ-Δ-Δ 0.024 mM furfuraldehyde. □-□-□ 0.036 mM furfuraldehyde.

from zincate solutions revealed that zincate solutions undergo successive reduction to zinc. The chemical step followed by first electron transfer is the slow step. Triethanolamine was adsorbed on the electrode surface and hindered the rate of zinc deposition. Presence of triethanolamine and furfuraldehyde in zincate solutions hindered the hydrogen evolution reaction.

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