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ROLE OF ALDEHYDES ON THE ELECTROCHEMICAL DEPOSITION AND DISSOLUTION OF ZINC: A CYCLIC VOLTAMMETRIC STUDY

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ABSTRACT

Electrochemical deposition and dissolution of zinc in acidic zinc plating bath solutions containing formaldehyde (FA), benzaldehyde (BA) or furfuraldehyde (FUA) has been studied by cyclic voltammetric technique. Shapes of voltammograms, peak potentials and Tafel slopes are not affected by the presence of aldehydes in the plating bath solution. Aldehydes decreased the peak currents and the extent of decrease is in the order: FUA>BA>FA. This is accounted by Langmuir type of adsorption of aldehydes on zinc-solution interface and the electron density of oxygen atoms in aldehydes. SEM photographs of zinc deposits indicated the gradual decrease of grain size from FA to BA and FUA. Negative values of ΔS_a° and ΔG_a° suggested the considerable interaction of aldehydes on zinc surface with rigid adsorbed species.

Keywords: Cyclic voltammetry, zinc-dissolution-deposition, aldehydes, surface adsorption.

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INTRODUCTION

Additives in trace concentrations affect both deposition and dissolution of metals. They participate so decisively [1] and understanding of their actions require knowledge of adsorption of these additives at metal-solution interface [2, 3]. Zinc coating is extensively used world over to protect iron and mildsteel from corrosion [4]. Aldehydes are added to zinc plating baths to obtain bright deposits and addition of furfuraldehyde to alkaline tartarate bath helped to obtain slate gray deposit [5]. A cyclic voltammetric technique has been used in understanding the role of additives during plating of nickel [6] and zinc [7]. The present communication reports the results pertaining to cyclic voltammetric investigation of role of FA, BA and FUA on the dissolution and deposition of zinc.

EXPERIMENTAL

The solutions were prepared using distilled water and analytical grade chemicals. An all glass three electrode cell assembly of 50mL capacity was used for the voltammetric studies. A platinum wire (0.05 cm^2), a large platinum foil and a saturated calomel electrode were used as working, counter and reference electrodes respectively. The platinum electrodes were pre-cleaned by the regular procedure [8]. To minimize IR drop, a finely drawn luggin 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). The solutions were prepared by various concentrations of FA, BA and FUA ($5 \times 10^{-5} < X > 1 \times 10^{-3} \text{ M}$) using 0.01M sodium sulphate as supporting electrolyte at various temperatures. The pH of the solution was maintained at 3.0 using dilute sulphuric acid. The voltammograms were recorded after obtaining reproducible traces on repeated scanning.

RESULTS

Cyclic voltammetric experiments were carried out in a zinc plating bath solution ($2 \times 10^{-2} \text{ M ZnSO}_4 + 1 \times 10^{-2} \text{ M Na}_2\text{SO}_4$) at a temperature 298K, pH 3.0 and different scan rates. The electrode was polarized from -1500 mV (cathodic termination potential $-E_{\lambda c}$) to $+100 \text{ mV}$ (Anodic termination potential $-E_{\lambda a}$). The forward scan exhibited a cathodic

peak at -1120 mV (Fig. 1) which became active with sweep rate in the range 10-100 mV/s. The reverse scan exhibited a small peak at -875 mV followed by a distinct anodic peak at -785 mV . The anodic peak potentials became more positive with sweep rate.

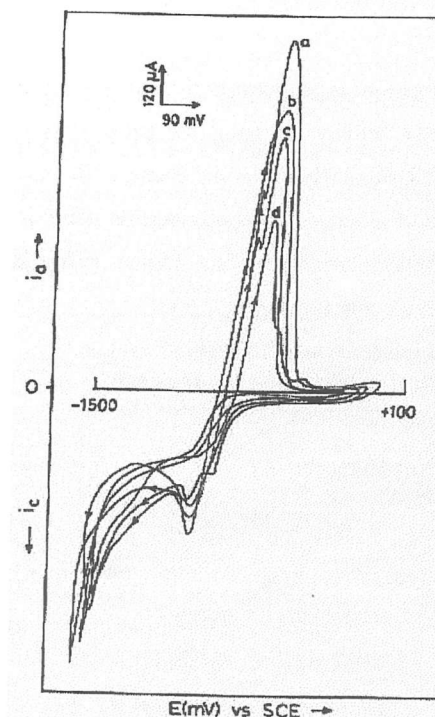


Fig.1 Cyclic voltammograms obtained in zinc plating bath solution ($2 \times 10^{-2} \text{ M ZnSO}_4 + 1 \times 10^{-2} \text{ M Na}_2\text{SO}_4$) [a] with $1 \times 10^{-3} \text{ M FA}$ [b], $1 \times 10^{-3} \text{ M BA}$ [c] and $1 \times 10^{-3} \text{ M FUA}$ [d] at the scan rate 10 mv/s, temperature 298k and pH 3.0.

Zero current crossing potential (zccp) was found to be 985 mV. Sweep rate had no influence on the shape of the voltammogram.

Introduction of 10^{-3} M different aldehydes (FA, BA and FUA) did not modify the voltammogram. When FA was added, the forward scan exhibited a peak at -1120 mV followed by hydrogen evolution. A sharp peak appeared at -875 mV as noticed in the

The voltammograms obtained at 10mVs^{-1} were used to get Tafel slopes for anodic and cathodic reactions. The potential values obtained from the foot of the wave up to peak potentials were taken and plotted vs $\log i$. Anodic and cathodic Tafel slopes were found to be $30 \pm 5 \text{ mV/decade}$ and $130 \pm 10 \text{ mV / decade}$ respectively. These values are invariant with the addition of aldehydes to the zinc plating bath solution.

In the present investigation it is noticed that aldehydes decreased the peak currents (anodic and cathodic) without affecting the peak potentials. The extent of decrease of anodic peak current was higher than the extent of decrease of cathodic peak current with the concentration of aldehyde. This observation is the indication of surface adsorption of aldehydes at metal-solution interface. Hence, it was decided to evaluate some parameters related to surface adsorption.

Table 1: Anodic peak currents and θ values at various concentrations of aldehydes at the scan rate 10 mV/s

Aldehyde M	Peak Current (μA)		
	FA	BA	FUA
5×10^{-5}	1491(0.08)	1061(0.37)	790(0.51)
1×10^{-4}	1060(0.34)	750(0.53)	470(0.71)
2.5×10^{-4}	770(0.52)	645(0.66)	323(0.80)
5×10^{-4}	630(0.61)	410(0.74)	174(0.89)
1×10^{-3}	535(0.67)	320(0.80)	110(0.93)

The surface coverage (θ) values are calculated (Table 1) from the peak currents of the voltammograms obtained with (i_p^*) and without (i_p) aldehydes in the solution using the equation

$$\theta = 1 - (i_p^* / i_p) \quad (1)$$

The values of θ are plotted against the concentration of aldehydes (Fig.3). An examination of these data confirms that the adsorption of aldehydes follows Langmuir type of adsorption isotherm, which fits into the relation [9],

$$C/\theta = 1/K + C \quad (2)$$

From the plots of C/θ vs C ; K values for different aldehydes (Fig. 4) were evaluated (Table 2).

The standard Gibbs energy change (ΔG_a°) for adsorption was calculated for each aldehyde using equation [10].

$$\Delta G_a^\circ = -RT \ln (55.5 K) \quad (3)$$

Entropy of adsorption (ΔS_a°) was calculated from the plots of ΔG_a° vs T [11]. Enthalpy of adsorption (ΔH_a°) was evaluated by using Gibbs-Helmholtz equation [12]. These thermodynamic values for adsorption of aldehydes at Zn-solution interface are given in Table 2.

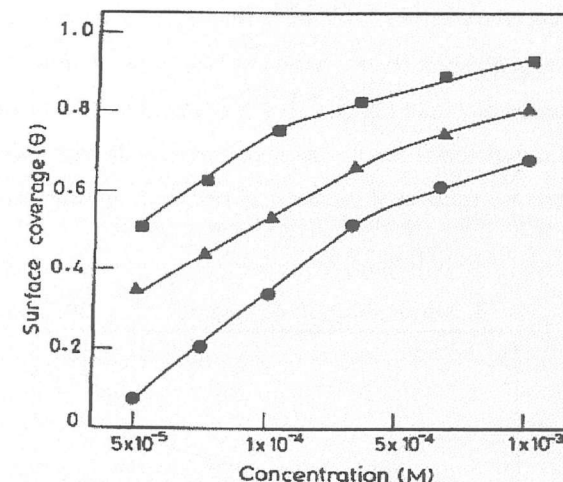
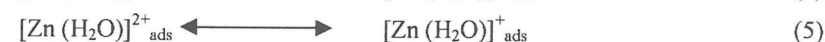
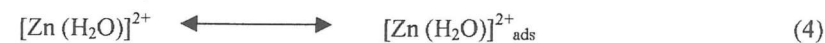
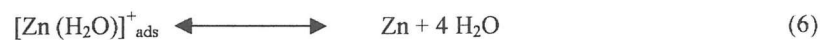


Fig.3 Plots of surface coverage against concentration (M)
O-FA, Δ -BA and \square - FUA

DISCUSSION

Under transient polarization conditions, in zinc sulphate solution at pH 3, the deposition of zinc may involve monovalent zinc ions which is further confirmed by the observed results, $d \log i_{p,c} / d \log \text{Zn}^{2+}$ as 0.54.





For a slow first electron transfer step, the cathodic current i_c is given by the equation

$$i_c = k_2 \left(\frac{k_1}{k_1} \right) [\text{Zn}(\text{H}_2\text{O})^{2+}] \exp / -\alpha_c F \Delta \phi_c / RT \quad (7)$$

where α_c is the cathodic transfer coefficient; $\Delta \phi_c$ is the interfacial potential difference. k_1 and k_2 are the rate constants of backward and forward reactions. If the discharge of zinc ions are irreversible [13], then

$$E_{p,c} = E^0 + RT/nF \{ \ln k_0 / D^{1/2} - 0.5 \ln (-\alpha_c F v / RT) - 0.78 \} \quad (8)$$

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 $2.303 RT / (-\alpha_c F)$ and the observed value of $130 \pm 10 \text{ mV/decade}$ as Tafel slope confirms. In a similar way one could expect an anodic Tafel slope of $30 \pm 5 \text{ mV/decade}$. This is also in conformity with the observed experimental result. The appearance of distinct anodic peaks during reverse scan suggests the stepwise dissolution of zinc from different energy sites on the surface.

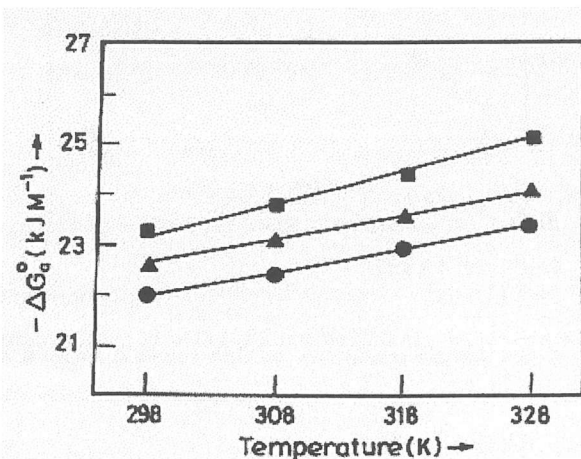


Fig.4 Plots of $-\Delta G^0$ (free energy of adsorption) vs temperature (K)
O-FA, Δ-BA and □-FUA

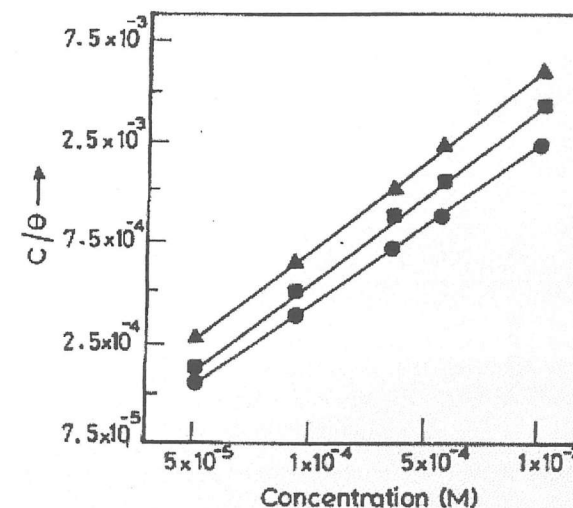


Fig.5 Plots of C/θ against θ
Δ-FA, □-BA and O-FUA

In the presence of aldehydes, peak potentials and Tafel slopes (anodic and cathodic) were invariant. However, peak current decreases with increase in concentration of aldehydes. Surface coverage increases exponentially with the concentration of aldehydes (Fig. 3). These results suggest that aldehydes do not participate in the dissolution and deposition reaction and retard the reaction rates by simple surface adsorption process.

Table 2: Thermodynamic Properties of adsorption of the aldehydes

Aldehyde	$-\Delta G_a^0$	$-\Delta H_a^0$	$-\Delta S_a^0$	K
M	KJM ⁻¹	KJM ⁻³	JK ⁻¹ M ⁻¹	M ⁻¹
FA	22	13.4	45.1	7x10 ³
BA	22.6	16.2	54.3	9x10 ³
FUA	23.1	23.3	78.1	11x10 ³

The adsorption of these aldehydes is due to the interaction of lone pair of electrons on the oxygen atoms of the molecules with the zinc surface. The extent of adsorption and decrease of peak current depend on the electron density on the oxygen

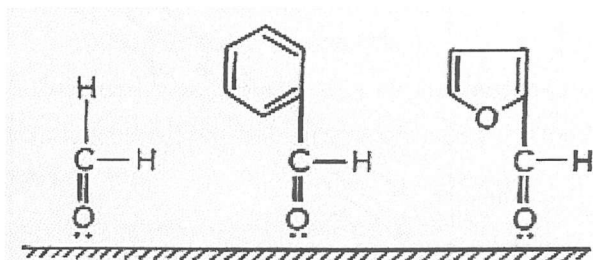


Fig.6A. Mode of adsorption of aldehydes on zinc surfac

atom. Among the aldehydes studied, the electron density on the oxygen atoms of aldehydes is in the order

$$FUA > BA > FA$$

which is in agreement with the surface coverage values observed (Table 1) under comparable experimental conditions.

The calculated values of ΔG°_a for different aldehydes are negative and nearly in the same magnitude which indicate the common mode of adsorption and strong interaction on zinc surface (Fig. 6A). ΔS°_a for FA is less negative whereas FUA is more negative. SEM photographs of zinc deposits obtained from zinc plating bath solution without and with aldehydes (Fig. 6B) revealed that the grain size of the deposit decreased in the order of addition of FA, BA and FUA respectively.

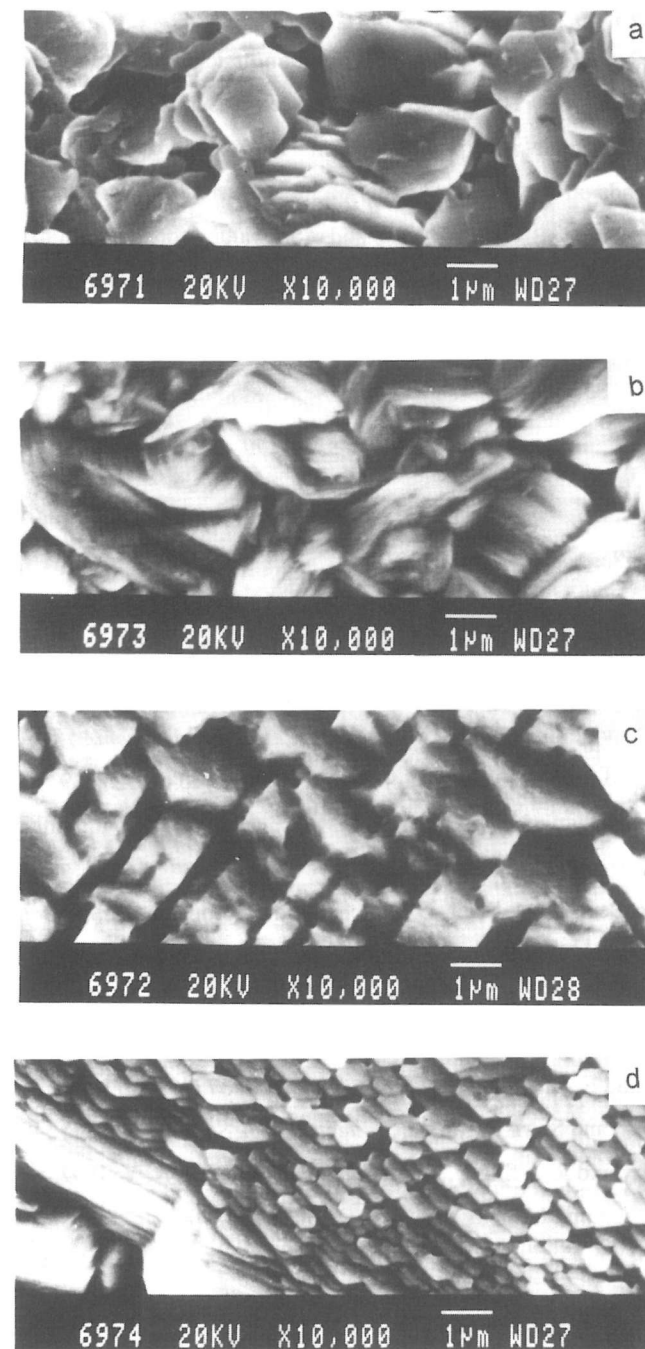


Fig.6B. SEM photographs of zinc deposits (a) Without aldehydes, (b) 1×10^{-3} M FA, (c) 1×10^{-3} M BA and (d) 1×10^{-3} M FUA

CONCLUSIONS


Mechanism of zinc deposition or dissolution in acidic solution is not affected by the presence of aldehydes. The reactions are retarded by surface adsorption of aldehydes, which follows Langmuir adsorption isotherm. The extent of adsorption or reaction retardation depends on the electron density on the oxygen atoms in the molecules which is in the order FUA > BA > FA. ΔG_a° and ΔS_a° values for adsorption processes are negative which suggests considerable interaction of aldehydes on zinc surface.

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