

## Electrochemical behaviour of zinc gluconate complexes

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**Abstract.** Voltammetric studies revealed that under transient conditions in the pH range 3.7 to 5.0, the deposition of zinc from ZnSO<sub>4</sub> solutions involves the formation of adsorbed monovalent zinc. The conversion of divalent zinc to monovalent is a slow step. In the presence of gluconate, the reduction of divalent complex involves the monovalent zinc complex and the second electron transfer is slow. In the pH range 10 to 12.5, the zinc complex may be  $[\text{Zn}(\text{GH}_4)_4]^{2-}$  and is found to vary with gluconate and OH<sup>-</sup> ions. The conversion of  $[\text{Zn}(\text{GH}_4)(\text{OH})_{\text{ads}}]^-$  to Zn(OH)<sub>2</sub> or Zn(GH<sub>4</sub>)<sub>2</sub> is the slow step in the reduction of the complexes. In strong alkali solutions sodium gluconate forms zinc hydroxy gluconate complexes.  $[\text{Zn}(\text{OH})_3(\text{GH}_4)]^{2-}$  to adsorbed  $[\text{Zn}(\text{OH})(\text{GH}_4)]^-$  is the slow step in the reduction.

**Keywords.** Cyclic voltammetry; zinc complexes; gluconate complexes; electrochemical reduction.

### 1. Introduction

Gluconates have found use in zinc plating baths to give semibright and smooth deposits of zinc (Chester and Reisinger 1948; Chester 1952, 1953). Zinc gluconate complexes are of low stability and the stabilization is by the carboxylate group of the ligand in acid medium (Sawyer 1964). Zinc is deposited from sodium gluconate solutions from near neutral pH range. The presence of sodium gluconate produced good quality electrodeposits in highly alkaline noncyanide zinc plating baths compared to those from cyanide baths (Geduld 1990).

The present investigation aims at determining the following,

- (i) The nature and the reduction of zinc species in the pH range 3.7 to 5.0,
- (ii) The role of gluconate ions and OH<sup>-</sup> ions in the deposition of zinc from dilute alkali solutions and the nature of the zinc species,
- (iii) In high alkali solutions whether the deposition of zinc is from zinc hydroxy or zinc gluconate complex or zinc hydroxy gluconate complex.

### 2. Experimental

Triangular potential sweep experiments were carried out on Bio-analytical Systems 100 A, USA using a conventional three electrode cell assembly of glassy carbon as

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working, platinum as counter and saturated calomel electrode as reference electrodes respectively. The solutions under study were deoxygenated for one hour using purified hydrogen. The temperature of the cell was kept at  $30 \pm 0.01^\circ\text{C}$ .

*pH range 3.7 to 5:*  $\text{ZnSO}_4$  solutions ( $2.5 \times 10^{-2} \text{ M} <x> 10^{-1} \text{ M}$ ) with  $10^{-1} \text{ M Na}_2\text{SO}_4$  concentration to keep the ionic strength constant were used. The *pH* of the solution was monitored using a digital *pH* meter by adding a few drops of dilute  $\text{H}_2\text{SO}_4$  solution. Cyclic voltammograms were obtained from  $-1700 \text{ mV}$  to  $-500 \text{ mV}$ .

*pH range 10 to 12.5:*  $2.5 \times 10^{-2} \text{ M ZnSO}_4$  solutions were used. To this solution different concentrations of sodium gluconate ( $5 \times 10^{-1} \text{ M}$  to  $2 \text{ M}$ ) were added. The *pH* of the solution was monitored using a digital *pH* meter by adding a few drops of  $\text{NaOH}$ . Cyclic voltammograms were obtained from  $-1800 \text{ mV}$  to  $-1000 \text{ mV}$ .

Solutions above *pH* 12.5:  $5 \times 10^{-2} \text{ M ZnSO}_4$  concentration was used. To the above solution, different concentrations of sodium gluconate ( $2.5 \times 10^{-2} \text{ M} <x> 10^{-1} \text{ M}$ ) were added. The *pH* of the solutions were raised using  $\text{NaOH}$  to above 13. Cyclic voltammograms were obtained from  $-2000 \text{ mV}$  to  $-800 \text{ mV}$ . The sweep rates were restored to 5 to  $100 \text{ mV s}^{-1}$ .

### 3. Results

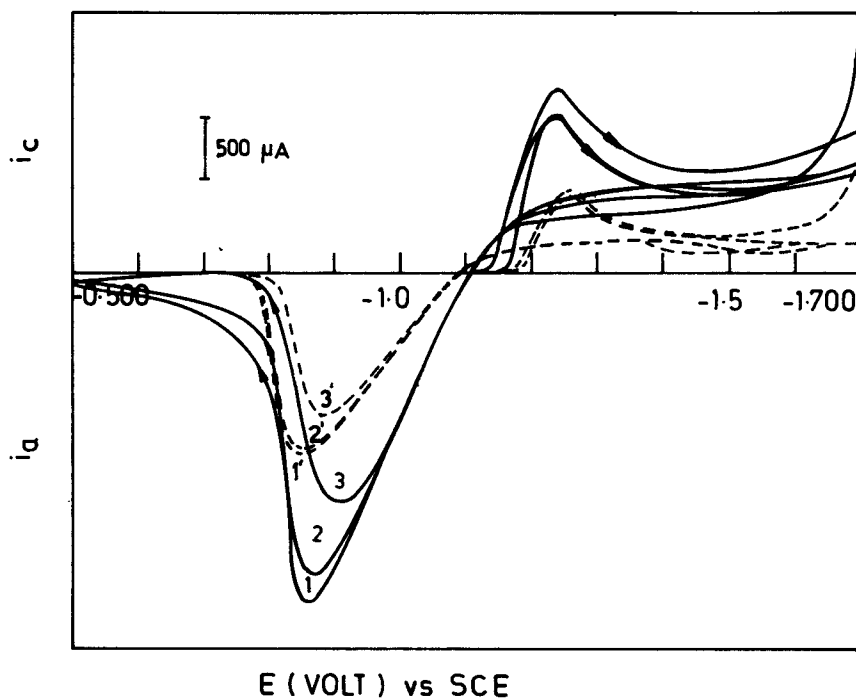
#### 3.1 *pH range of 3.7 to 5*

Figure 1 presents the electrochemical spectrum corresponding to polarisation from  $-1700 \text{ mV}$  to  $-500 \text{ mV}$  in  $\text{ZnSO}_4$  solutions. During the forward scan the zero current crossing potential occurred at  $-1100 \text{ mV}$  followed by an anodic peak at  $-886 \text{ mV}$ . The  $E_{p,a}$  (anodic peak potential) was found to vary with  $\log v$ . On repetitive cycling the  $E_{p,a}$  was found to shift towards negative direction. The current became minimum at  $-800 \text{ mV}$ . The reverse scan exhibited a sharp rise in current at  $-1190 \text{ mV}$  followed by a cathodic peak. The hydrogen evolution reaction was found to take place beyond  $-1600 \text{ mV}$ . The cathodic peak potential [ $E_{p,c}$ ] was found to vary with  $\log v$  and become negative with cycling. The cathodic peak potential varied with  $\log v$  and was independent of scan number (i.e. number of cycles).

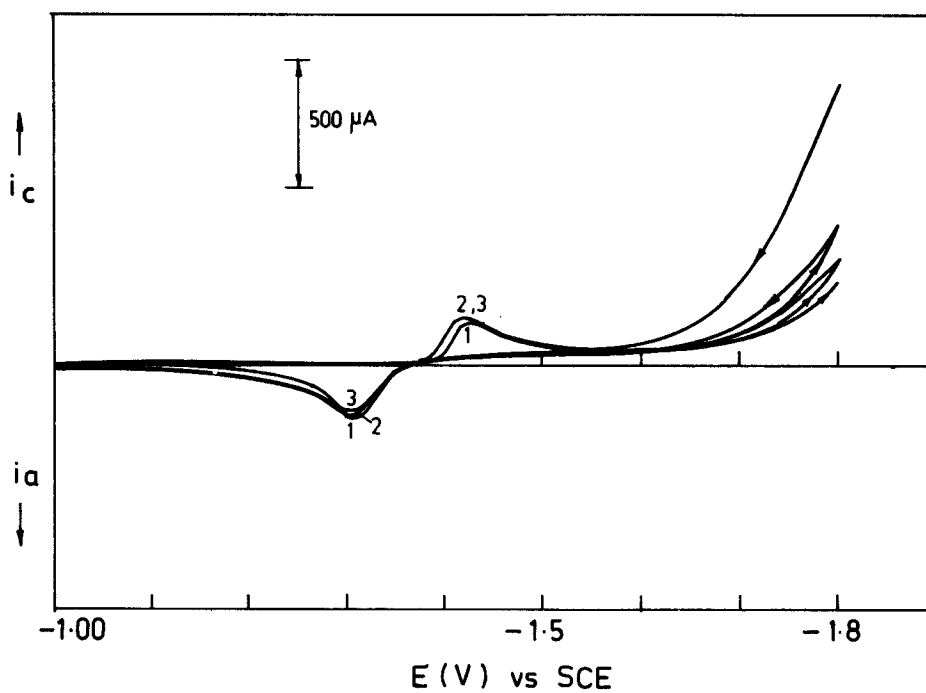
In presence of the complexing anions, the electrochemical spectrum exhibited no marked change. The anodic peak potential was found to vary with  $\log v$  and became negative with cycling. The cathodic peak potential varied with  $\log v$  and was invariant with scan number. The  $\Delta E_p = (E_{p,c} - E_{p,a})$  was found to vary with gluconate ion concentration suggesting that it takes part in the redox process.

#### 3.2 *pH range 10 to 12.5*

Figure 2 presents the electrochemical spectrum of  $2.5 \times 10^{-2} \text{ M ZnSO}_4$  containing  $2 \text{ M}$  sodium gluconate at *pH* 12.5. When polarised from  $-1800 \text{ mV}$  to  $-1000 \text{ mV}$ , in the forward scan an anodic peak appeared at  $-1306 \text{ mV}$ . The reverse scan exhibited a cathodic peak at  $-1426 \text{ mV}$  followed by hydrogen evolution at  $-1700 \text{ mV}$ . Increase of scan number shifted the  $E_{p,c}$  to more negative values while  $E_{p,a}$  remained the same. The charges flowing under the cathodic peaks increased while those of anodic peaks decreased with scan number suggesting that the dissolution is hindered on subsequent



**Figure 1.** Cyclic voltammogram in  $10^{-1}$  M  $\text{Na}_2\text{SO}_4$  solution at pH 5; (i)  $5 \times 10^{-2}$  M  $\text{ZnSO}_4$ ; (ii)  $5 \times 10^{-2}$  M  $\text{ZnSO}_4 + 5 \times 10^{-2}$  M solution gluconate;  $E_{\lambda,a} = -500$  mV;  $E_{\lambda,c} = -1700$  mV;  $v = 10$  mV s $^{-1}$ ; 1, 2, 3 scan numbers.



**Figure 2.** Cyclic voltammogram in  $2.5 \times 10^{-2}$  M  $\text{ZnSO}_4 + 2$  M sodium gluconate at pH 12.5;  $v = 10$  mV s $^{-1}$ .

cycling. The  $E_{p,c}$  shifted to more positive values with log sweep rate with a slope of  $60 \pm 5 \text{ mV decade}^{-1}$  and an increase of pH shifted them to more negative values suggesting that the deposition is favoured with increase of  $\text{OH}^-$  ions. The  $E_{p,c}$  moved towards more positive values with increase of gluconate concentration above 1.0 M, suggesting that the reduction of the zinc complex is hindered by the presence of gluconate. The anodic peak potentials shifted to more negative values with sweep rate and a plot of  $E_{p,a}$  vs  $\log v$  gave a value of  $60 \pm 10 \text{ mV decade}^{-1}$ . The pH rise caused the  $E_{p,a}$  to move towards more negative values suggesting that the dissolution of zinc is hindered by  $\text{OH}^-$  ion concentration rise while it was favoured by gluconate concentration as indicated by the shift of  $E_{p,a}$  to less negative potentials.

### 3.3 Higher alkali solutions

In 2 M NaOH +  $5 \times 10^{-2}$  M  $\text{ZnSO}_4$  solution, when polarised from  $-2000$  mV to  $-800$  mV, the forward scan exhibited an anodic peak at  $-1322$  mV. A cathodic peak was observed at  $-1484$  mV followed by hydrogen evolution on the reverse scan (figure 3). Increase of scan number shifted the  $E_{p,a}$  to less negative values and  $E_{p,c}$  to more positive values. The charges flowing under the cathodic peak increased while those of anodic peaks decreased suggesting that the dissolution of zinc was hindered on cycling. Upto  $5 \times 10^{-2}$  M  $\text{ZnSO}_4$  concentration the  $E_{p,a}$  was invariant with sweep rate and became negative with increasing  $\text{ZnSO}_4$  concentration. The  $E_{p,a}$  varied with log sweep rate with a slope of  $50 \pm 20 \text{ mV decade}^{-1}$  while the  $E_{p,c}$  varied with  $\log v$  at all  $\text{ZnSO}_4$  concentrations with a slope of  $45 \pm 15 \text{ mV decade}^{-1}$ .

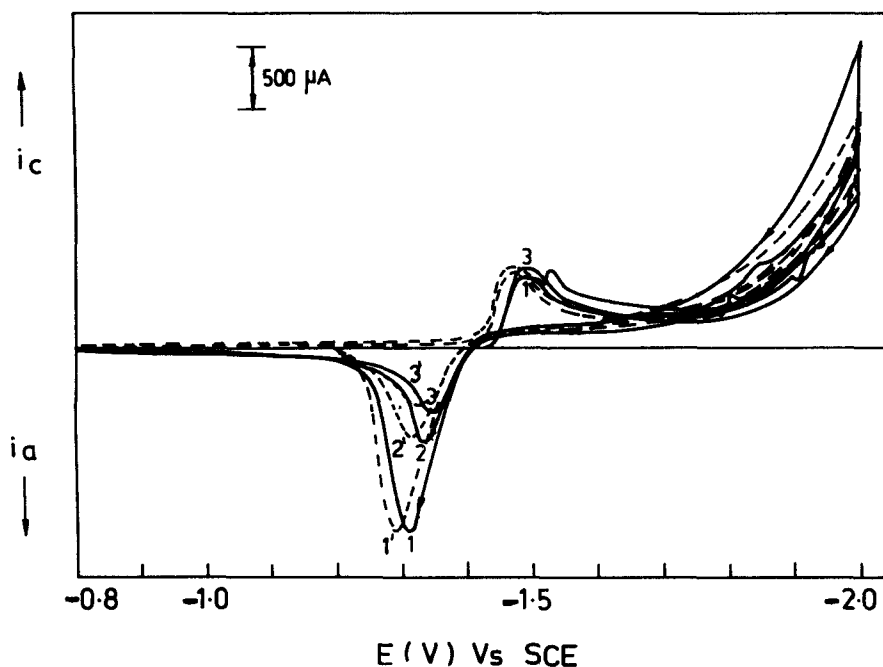


Figure 3. Cyclic voltammogram in 2 M NaOH solutions; (i)  $5 \times 10^{-2}$  M  $\text{ZnSO}_4$ ; (ii)  $5 \times 10^{-2}$  M  $\text{ZnSO}_4$  +  $2.5 \times 10^{-2}$  M sodium gluconate;  $v = 10 \text{ mV s}^{-1}$ .

In presence of the complexing anions, the electrochemical spectrum exhibited interesting features. With  $2.5 \times 10^{-2}$  M sodium gluconate, the forward scan exhibited an anodic peak at  $-1302$  mV which was less positive to the peak potentials observed in absence of sodium gluconate. On reversing the scan, a cathodic peak appeared at  $-1498$  mV followed by hydrogen evolution. This cathodic peak appeared 10 mV more negative to the peak potential observed in absence of sodium gluconate suggesting the participation of gluconate ion in the complex formation. Increase of scan number shifted the  $E_{p,a}$  to positive values while the  $E_{p,c}$  was invariant with scan number. The cathodic charge increased with cycling while the anodic charge decreased suggesting that the dissolution is hindered on cycling.

Increase of sodium gluconate concentration shifted the  $E_{p,a}$  and  $E_{p,c}$  to more negative values suggesting that gluconate ion hinders the dissolution process and favours deposition. The anodic and cathodic peak potentials varied linearly. The anodic and cathodic peak potentials varied linearly with gluconate concentration and log sweep rate.

Increase of NaOH concentration above 1 M shifted the  $E_{p,a}$  to more positive values suggesting that the dissolution of zinc is favoured by  $\text{OH}^-$  ions. They varied by 120 mV with a decade change of  $\text{OH}^-$  ions. The  $E_{p,c}$  shifted to more positive values with  $\text{OH}^-$  ion suggesting that the deposition is hindered.

#### 4. Discussion

$\text{Zn}/\text{Zn}^{2+}$  reaction ranks along with the hydrogen and oxygen evolution reactions as one of the extensively studied reactions. In non-complexing solutions, a reversible two electron transfer process and multiple polarographic waves were associated with various complexes in solution with zinc (Bard 1976).

##### 4.1 Behaviour in the pH range 3.7 to 5

The deposition of zinc under transient conditions ( $5$  to  $100$   $\text{mV s}^{-1}$ ) may involve the formation of  $\text{Zn}^+$  and



would result

$$i_c = \bar{K}_2 (\bar{K}_1 / \bar{k}_1) [\text{Zn}^{++}] \exp - \alpha_c F \Delta\phi / RT \quad (4)$$

where  $\alpha_c$  is the cathodic transfer coefficient,  $\Delta\phi$  is the interfacial potential difference and  $\bar{K}$  and  $\bar{K}$  are the rate constants of forward and backward reactions.

If the discharge is irreversible (as there is anodic and cathodic peak separation [Nicholson and Shain 1964; Macdonald 1977])

$$E_{p,c} = E^0 + RT/nF (\ln K^0 / \sqrt{D} - 0.5 \ln \alpha F v / RT - 0.78) \quad (5)$$

where  $E_{p,c}$  is the cathodic peak potential;  $v$  is the sweep rate;  $D$  is the diffusion coefficient of the  $Zn^{++}$  ions.

The plot of  $E_{p,c}$  vs  $\log v$  would give cathodic Tafel slope and the observed cathodic Tafel slope of  $110 \pm 10$  mV decade<sup>-1</sup> suggests that the first electron transfer is slow.

$$i_{p,c} = [nFA C_{Zn^{++}}^0 \sqrt{\pi D_0} (\alpha v / RT) (E_i - E)] \quad (6)$$

where  $E_i$  is the initial potential and  $C_{Zn^{++}}^0$  is the concentration of the  $Zn^{++}$  species undergoing reduction.

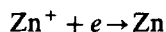
$$\left( \frac{d \log i_{p,c}}{d \log C_{Zn^{++}}^0} \right)_v$$

would give the reaction order w.r.t  $Zn^{++}$  ion.

The observed

$$\left( \frac{d \log i_{p,c}}{d \log (Zn^{++})} \right)_v = 0.9 \pm 0.1$$

suggests that



is the slow step.

Gluconic acid is represented (Pecsok and Juvet 1955) by  $HGH_4$  where the first H refers to the carboxylic acid hydrogen and  $H_4$  refers to the four hydrogens on the secondary alcohols. The anion of the gluconic acid is represented as  $GH_4^-$ . It was shown earlier that zinc forms gluconate complex in the acid range and the divalent complex  $[Zn(GH_4)]^+$  has stability constant of  $\log K = 1.7 \pm 0.05 \times 10^{-4}$ . The anodic and cathodic peak currents were independent of pH at all sweep rates studied. This suggests that  $OH^-$  ions do not participate in the reaction scheme. The gluconate additions greatly influenced the anodic peak currents while cathodic peak currents were invariant with gluconate concentration.

One may visualise in presence of gluconate,



where  $GH_4^-$  is the gluconate anion.

Under Langmuir conditions, if the conversion of the divalent complex to the monovalent one is slow,

$$i_c = \bar{K}_1 [Zn(GH_4)]^+ \exp - \beta F \Delta \phi / RT, \quad (9)$$

and if the second electron transfer is slow

$$i_c = \bar{K}_2 K_1 [Zn(GH_4)]^+ \exp - (1 + \beta) F \Delta \phi / RT. \quad (10)$$

If the surface coverage  $\theta > 0.1$  and for the non activated Temkin isotherm with

**Table 1.** Possible schemes and expected values for the deposition/dissolution of zinc from zinc-gluconate complexes under Langmuir condition.

Scheme	Tafel slope (mV/decade)		$\left\{ \frac{d \log i_{p,a}}{d \log (\text{GH}_4^-)} \right\}_{\text{pH}, \text{Zn}^{2+}}$
	Anodic	Cathodic	
$\text{Zn}(\text{GH}_4)^+ + e \rightarrow \text{Zn}(\text{GH}_4)$ $\text{Zn}(\text{GH}_4) + e \rightleftharpoons \text{Zn} + (\text{GH}_4^-)$	40	120	1.0
$\text{Zn}(\text{GH}_4)^+ + e \rightleftharpoons \text{Zn}(\text{GH}_4)$ $\text{Zn}(\text{GH}_4) + e \rightarrow \text{Zn} + (\text{GH}_4^-)$	120	40	1.0

Experimental:

$$\left\{ \frac{d E_{p,a}}{d \log v} \right\} = 140 \pm 10 \text{ mV/decade}$$

$$\left\{ \frac{d \log i_{p,a}}{d \log (\text{GH}_4^-)} \right\}_{\text{pH}, \text{Zn}^{2+}} = 0.5.$$

the second electron transfer

$$i_c = \bar{K}_2 K_1 \{ (\text{Zn}(\text{GH}_4)^+ )^{0.5} \exp - \beta F \Delta \phi / RT, \quad (11)$$

and

$$i_a = \bar{K}_1 [\text{Zn}] [\text{GH}_4^-] \exp(1 - \beta) F \Delta \phi / RT. \quad (12)$$

Under transient conditions, possible schemes and the expected values for the deposition of zinc from zinc-gluconate complexes in the pH range 3.7 to 5 are given in the table 1.

In the pH range studied some of the gluconate might have been converted to  $\delta$ -lactone and  $\gamma$ -lactone. The reported equilibria are

$$\frac{(\text{H}^+)(\text{GH}_4^-)}{(\text{HGH}_4) + (\text{L})} = [1.76 \pm 0.05] \times 10^{-4} \quad (13)$$

and 13% of the gluconic acid would have been converted to lactones and the release of  $(\text{GH}_4^-)$  is restricted by the  $pK_a$  values of the gluconic acid. Hence  $\{d \log i_{p,a} / d \log (\text{GH}_4^-)\}$  was found to be 0.5 instead of 1 as expected.

#### 4.2 Behaviour in the pH range 10.0 to 12.5

Consider a general form of zinc gluconate complex formation at equilibrium as



where M represents  $\text{Zn}^{2+}$  species; L is a ligand  $\text{GH}_4^-$  or gluconate ion and  $\text{ML}_n$  is the complex in a molar ratio 1 to n for M and L.

The molar ratio A can be defined as

$$A = \left[ \left\{ \sum_{n=1}^N n(\text{ML}_n) + (\text{L}) \right\} \div C_M \right] \quad (15)$$

where N is the maximum co-ordination number and  $C_M$  is the metal ion concentration.

If  $A$  is smaller than  $N$  just before the equivalence point,  $C_M$  and  $[L]$  are expressed as

$$C_M = [ML_{n-1}] + [ML_n] \text{ and } [L] = 0 \quad (16)$$

Hence

$$A = \frac{N - (ML_{n-1})}{(ML_{n-1}) + (ML_n)} \quad (17)$$

$$ML_{n-1} = (N - A)C_M \text{ and}$$

$$ML_n = (A - N + 1)C_M. \quad (18)$$

In cyclic polarisation experiments the cathodic peak current at a given sweep rate is

$$i_{p,c} = Kc_1(ML_{n-1}) + Kc_2(ML_n) \quad (19)$$

and

$$Kc_1 \text{ and } Kc_2 \text{ are constants.}$$

Substituting

$$i_{p,c} = (Kc_2 - Kc_1)AC_M + \{(Kc_1 - Kc_2)N + Kc_2\}C_M \quad (20)$$

$i_{p,c}$  and  $A$  curves were used earlier to find out the composition of the complexes (Ogura *et al* 1980; Ogura 1984).

Table 2 presents the  $i_{p,c}$  vs  $A$  i.e., [gluconate/zinc metal] ratio for zinc gluconate complexes. It may be seen that after a value of  $A = 4$ ,  $i_{p,c}$  becomes independent of  $A$  suggesting that the complex has 4 gluconate ions as ligands. The cathodic peak currents were found to be independent of pH rise indicating the absence of  $\text{OH}^-$  ions in the zinc complex.

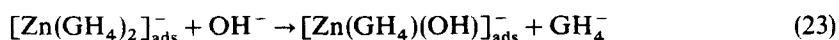
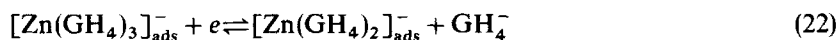
The deposition of zinc under transient conditions may involve adsorbed intermediates

**Table 2.** Variation of cathodic peak current with  $A$  in pH range 10 to 12.5.

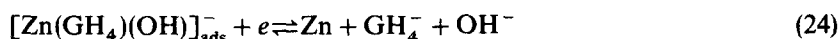
Sweep rate ( $\text{mV s}^{-1}$ )	$A = \left[ \frac{\text{gluconate}}{\text{zinc metal}} \right]$	$i_{p,c}$ (mA)
5	2	0.22
	4	0.13
	6	0.13
	8	0.13
10	2	0.31
	4	0.16
	6	0.16
	8	0.16
25	2	0.42
	4	0.20
	6	0.20
	8	0.20
50	2	0.54
	4	0.31
	6	0.31
	8	0.31



and the observed cathodic Tafel slope as obtained from  $(d E_{p,c}/d \log v) = 60 \pm 10 \text{ mV decade}^{-1}$  suggests that



and



Hence

$$i_c = \bar{K} [\text{Zn}(\text{GH}_4)_4]^{2-} \exp - \alpha_c F \Delta \phi / RT \quad (25)$$

and

$$i_a = \bar{K} (\text{Zn})(\text{GH}_4^-)^2 (\text{OH}^-)^{-1} \exp \alpha_a F \Delta \phi / RT \quad (26)$$

where  $\alpha_a$  and  $\alpha_c$  are transfer coefficients  $\Delta \phi$  is the interfacial potential difference under transient conditions.

$$\left\{ \frac{d \log i_{p,a}}{d \log (\text{GH}_4^-)} \right\}_{\text{OH}^-, v} = 2 \text{ and}$$

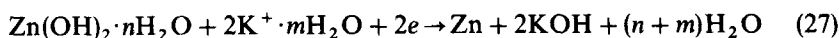
$$\left\{ \frac{d \log i_{p,a}}{d \log \text{OH}^-} \right\}_{v, \text{GH}_4^-} = 1.$$

The anodic peak currents were found to vary with pH with a value of  $0.78 \pm 0.02$ . The observed marginal dependency of  $E_{p,c}$  with unit pH rise may be due to the partial neutralisation of protons of the secondary alcohols by  $\text{OH}^-$  ions. The anodic and cathodic peak potentials were found to vary with gluconate ion concentration. However one would expect the  $E_{p,a}$  to shift towards more positive values with gluconate ion concentration. It was observed earlier (Pescok and Sandera 1957) in cadmium gluconate complex formation in the range of pH 8 to 12, the complex may become hydroxylated or the gluconate bound in the complex may lose  $\text{H}^+$  ions from the secondary alcohols. Cadmium gluconate complex was found to reach equilibrium after several hours and the nature of the complex was not known with certainty.

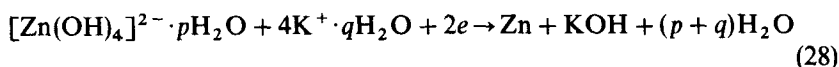
In this study  $[\text{Zn}(\text{OH})_4]^{2-}$  is likely to be formed along with zinc gluconate complex and equilibrium between them would have been slow. The real slow step may be the formation of  $[\text{Zn}(\text{OH})(\text{GH}_4)]^-$  and its subsequent conversion either to  $\text{Zn}(\text{OH})_2$  or  $\text{Zn}(\text{GH}_4)_2$  in the dissolution of reaction. Depending upon the critical ratio of gluconate to  $\text{OH}^-$  ions the composition of the complex may vary.

### 4.3 Behaviour in solutions of $\text{pH} \geq 12.5$

In an electrochemical reduction of complex species as is that of  $\text{Zn}(\text{II})$  present in alkaline solutions the overall reaction changes its stoichiometry with changing concentration of the ligand. Thus in dilute alkali solutions one would expect,



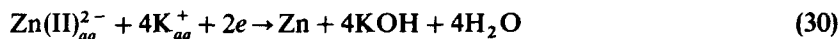
while at high hydroxide concentrations one would expect



or in general



where  $y$  and  $z$  are the average stoichiometric factors varying with NaOH concentration. It was shown earlier from potentiometric data (Dirkse 1954; Jovanovic *et al* 1973) that



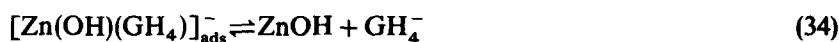
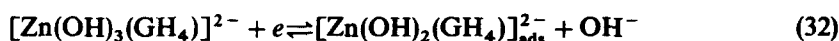
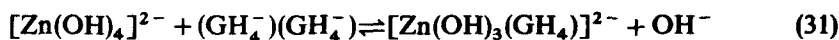
On this basis it was assumed that  $\{\text{Zn(II)}\}^{2-}$  in the tetrahydro complex seems to be stable at the highest KOH concentrations attainable i.e. it appeared not to exhibit any acidity. In the pH range 1 M to 7 M KOH solutions zinc exists as  $[\text{Zn(OH)}_4]^{2-}$  as revealed from IR and Raman spectral data (Fordyce and Brown 1965; Newman and Blomgren 1965).

At concentrations of sodium hydroxide  $< 3$  M (Gerisher 1956) the electroactive species was found to be  $\text{Zn(OH)}_2$ ; anodic dissolution of zinc amalgams revealed that  $\text{ZnOH}^+$  was the electroactive species (Stormberg and Trushima 1966; Stormberg and Popova 1967, 1968) and on solid zinc electrode  $[\text{Zn(OH)}_3]^-$  was found to be the electroactive species (Muralidharan and Rajagopalan 1978).

Table 3 presents the  $i_{p,c}$  vs  $A$  values for [gluconate/zinc ion concentration] ratio and  $[\text{OH}^-/\text{Zn}^{++}]$  ion concentration] ratios. Beyond a value of  $1.0$   $i_{p,c}$  were invariant with  $A$ . The  $i_{p,c}$  change gradually with  $A = 3$ , and beyond a value of 4 sudden fall was observed at all sweep rates for  $[\text{OH}^-/\text{Zn}^{++}]$  ratios.

In highly alkaline solution  $\gg 1$  M NaOH, the species that formed was  $[\text{Zn(OH)}_4]^{2-}$  and may undergo change in composition in presence of  $10^{-1}$  M sodium gluconate as  $[\text{Zn(OH)}_3(\text{GH}_4)]^{2-}$ .

The reduction of this complex may occur as



If step (33) is rds,

$$i_c = \bar{K} [\text{Zn(OH)}_4]^{2-} (\text{GH}_4^-) (\text{OH}^-)^{-2} \exp - F \Delta\phi / RT$$

where  $\bar{K}$  is the forward rate constant.

Under linear sweep conditions,

$$\left\{ \frac{d \log i_{p,c}}{d \log \text{OH}^-} \right\}_{v, \text{GH}_4^-} = -2 \text{ and,}$$

$$\left\{ \frac{d \log i_{p,c}}{d \log (\text{GH}_4^-)} \right\}_{v, \text{OH}^-} = +1,$$

$$E_{p,c} = \frac{2.303 RT}{F} \log K + \frac{2.303 RT}{F} \log \frac{[\text{Zn(OH)}_4]^{2-} (\text{GH}_4^-)}{(\text{OH}^-)^2}, \quad (36)$$

This suggests that  $[dE_{p,c}/d \log \text{OH}^-]_{v, \text{GH}_4^-} = -120 \text{ mV/decade}^{-1}$  and

$$[dE_{p,c}/d \log \text{GH}_4^-]_{v, \text{OH}^-} = 60 \text{ mV decade}^{-1}.$$

**Table 3.** Variation of cathodic peak currents with  $A$  in alkali gluconate solutions above pH 12.5.

Sweep rate (mV s <sup>-1</sup> )	$A = \left( \frac{\text{gluconate ion}}{\text{zinc metal}} \right)$		$A = \left( \frac{\text{hydroxide ion}}{\text{zinc metal}} \right)$	
	$A$	$i_{p,c}$ (mA)	$A$	$i_{p,c}$ (mA)
5	0.5	0.54	2	0.52
	1.0	0.6	3	0.52
	2.0	0.7	4	0.48
	3.0	0.7	6	0.37
10	0.5	0.6	2	0.65
	1.0	0.7	3	0.65
	2.0	0.7	4	0.65
	3.0	0.7	6	0.48
25	0.5	0.72	2	0.92
	1.0	0.81	3	0.92
	2.0	0.9	4	0.87
	3.0	0.9	6	0.70
50	0.5	0.78	2	1.20
	1.0	0.87	3	1.20
	2.0	0.87	4	1.20
	3.0	0.87	6	1.86

**Table 4.** Mechanistic parameters derived for the electrochemical reduction of zinc hydroxy gluconate complexes.

Parameters	Theoretical values (mV decade <sup>-1</sup> )	Experimental values (mV decade <sup>-1</sup> )
$[dE_{p,a}/d \log v]$	60	50 ± 15
$[d \log E_{p,c}/d \log v]$	60	60 ± 15
$[dE_{p,c}/d \log x^-]_{\text{OH}^-,v}$	60	90 ± 15
$[dE_{p,c}/d \log x^-]_{\text{OH}^-,v}$	-60	-150 ± 10
$(dE_{p,a}/d \log \text{OH}^-)_{v,x^-}$	-120	-120 ± 5
$(dE_{p,c}/d \log \text{OH}^-)_{x^-,v}$	-120	-140 ± 10
$(d \log i_{p,a}/d \log x^-)_{\text{OH}^-,v}$	1.0	0.15
$(d \log i_{p,a}/d \log \text{OH}^-)_{x^-,v}$	-2.0	-1.5

Here  $x^-$  is the gluconate ion.

Table 4 presents the mechanistic parameters obtained for the electrochemical reduction of zinc hydroxy gluconate complexes. The disagreement in the value of

$$\{d \log i_{p,c}/d \log (\text{GH}_4^-)\}_{v,\text{OH}^-}$$

may be due to the neutralisation of protons of the secondary alcohols of the gluconate with  $\text{OH}^-$  ion in highly alkaline solutions.

#### 4. Conclusion

(i) In the pH range 3.7 to 5.0 from ZnSO<sub>4</sub> solution, the deposition of zinc involves the formation of adsorbed monovalent zinc with the conversion of divalent zinc to monovalent zinc as a slow step. In presence of gluconate the reduction of divalent complex has the second electron transfer as a slow step.

(ii) In the pH range 10 to 12.5 the zinc complex has the composition [Zn(GH<sub>4</sub>)<sub>4</sub>]<sup>2-</sup> and this composition was found to vary with gluconate and OH<sup>-</sup> ions. The conversion of adsorbed [Zn(GH<sub>4</sub>)(OH)]<sup>-</sup> to [Zn(OH<sub>2</sub>)] or Zn(GH<sub>4</sub>)<sub>2</sub> is the slow step in the reduction of these complexes.

(iii) In highly alkaline solutions sodium gluconate forms zinc hydroxy gluconate complexes [Zn(OH)<sub>3</sub>(GH<sub>4</sub>)]<sup>2-</sup> and the conversion of adsorbed [Zn(OH)<sub>2</sub>(GH<sub>4</sub>)]<sup>2-</sup> to adsorbed [Zn(OH)(GH<sub>4</sub>)]<sup>-</sup> is the slow step in the reduction of these complexes.

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