POLAROGRAPHIC STUDIES OF THE COMPLEXES OF Cd (II) WITH GLUCONATE IONS

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The reductions of Cd (II) with gluconate ion have been studied in aqueous and aqueous-alkanol mixtures at 30°C & μ = 0.5. The reductions are reversible and diffusion controlled. The half wave potentials shifted to more negative values and the diffusion current decreased with increasing ligand concentration showing complex formation between Cd (II) and gluconate ions. The composition and stability constants have been determined by DeFord & Hume's method.

Various attempts have been made from time to time to use non-aqueous solvents in polarography. Sartori & Giacomello[1] and Zanko & Manusova[2] made the early attempts. Arthur & Lyons[3] have used methanol in the study of Cd (II) & Pb (II). Peracchio & Meloche[4] and Zlotowski & Kolthoff[5] have studied polarography of alkali metal ions in ethanol-water mixtures and Matsuyama[6] has investigated the change in diffusion currents of a dozen metal ions in ethanol-water mixtures. Jain[7] has investigated the interaction of Cd (II) with 4-amino antipyrine in aqueous-methanol mixtures. Polarographic study of Mn (II) ions in aqueous mixtures of ethylene glycol and propanol has also been reported by Jain & Gaur[8]. It has been observed that the diffusion coefficients. in most of the cases are comparatively smaller in aqueous & non-aqueous solvent mixtures.

Peasok & Juvet[9] have studied the polarography of gluconate ions with Cd (II) & Pb (II) and reported the formation of a single complex. The present study deals with the study of Cd (II)-gluconate complexes in aqueous & aqueous-alkanol mixtures.

Experimental

Reagent grade chemicals were used. Various solutions were prepared containing 0.5 mM of Cd (II) and 0.1 M to 0.4 M of the gluconate ion. The ionic strength was kept constant at μ = 0.5 by adding requisite amount of sodium perchlorate. Purified nitrogen was used for deaeration after pre-saturation with aqueous-alkanol mixture to be studied. H type cell containing agar–agar plug saturated with sodium chloride was used as the electrolytic vessel. The polarograms were obtained at 30 ± 0.01°C. The temperature was kept constant by using a Haake type ultra thermostat. The current-voltage curves were recorded with a manual set up and the dropping mercury electrode had the following characteristics : m = 1.7645mg/sec. and t = 3.64 sec. (open circuit). All the $E_{\frac{1}{2}}$ measurements refer to SCE as the non-polarisable electrode.

Results and Discussion

A single, well defined, reduction wave appeared in each case and $E_{\frac{1}{2}}$ shifted to more negative potentials. Plots of i_d vs $\sqrt{h}$ (h = effective height of mercury column) and i_d vs C_M (C_M is the metal ion concentration) were linear and passed through the origin, showing thereby that the reduction process is diffusion controlled. The plots of log $i/(i_d - i)$ vs $E_{d.e.}$ are linear with slopes of the order of 31 ± 2 mv which indicates the reversible nature of the electrode reaction for n = 2. The plots of $E_{\frac{1}{2}}$ vs $-\log C_X$ (C_X is the concentration of gluconate ion) are smooth curves indicating the formation of two or more complexes in equilibrium. Lingane's[10] method could not be applied and therefore, the percentage distribution and the stability constants have been calculated by DeFord & Hume's method as modified by Irving[11].

The values of the overall formation constants were computed graphically from the equations :—

$$1.\ F_0([X]) = \text{antilog}_{10}\left[\frac{0.4343nF}{RT}(E_{1/2})_s - (E_{1/2})_c + \log\frac{I_s}{I_c}\right]$$

$$2.\ F_1([X]) = \frac{F_o([X]) - \beta_o/f_{MX}}{C_X f_X}$$

$$3.\ F_2([X]) = \frac{F_1([X]) - \beta_1/f_{MX}}{C_X f_X}$$

$$4.\ F_3([X]) = \frac{F_2([X]) - \beta_2/f_{MX}}{C_X f_X}$$

$$5.\ F_4([X]) = \frac{F_3([X]) - \beta_3/f_{MX}}{C_X f_X}$$

where subscripts 'S' & 'C' refer to the aquated cadmium ion and the complex respectively, I_s/I_c is the ratio of the diffusion currents; β_o, β_1, β_2 & β_3 are the formation constants of the complex, C_X denotes the concentration of gluconate ion and 'f' the activity coefficient.

(a) Cd (II)–gluconate ion system in aqueous medium :

The polarographic characteristics and the F_j ([X]) values are presented in Table 1. Three complex species :

$[Cd\ (gluconate)]^+$, $[Cd\ (gluconate)_2]$ and $[Cd\ (gluconate)_3]^-$ are formed. The stability constants are presented in Table 2.

Table 1. Polarographic characteristics & F_j ([X]) values of Cd (II)–gluconate system in aqueous medium at 30°C.

Cd (II) = 0.5 mM μ 0.5

C_X (Moles)	i_d (Divs.)	$E_{1/2}$ (-V vs SCE)	$F_o([X])$	$F_1([X])$	$F_2([X])$	$F_3([X])$
0.00	73.5	0.5790	—	—	—	—
0.10	65 0	0.5920	3.07	20.68	46.80	—
0.15	61 0	0.5970	4.80	25.31	62.07	200.47
0.20	61.0	0.6020	7.04	30.20	71.00	195.00
0.25	61.0	0.6065	9 94	35.78	79.12	188.00
0.30	61.0	0.6110	14.05	43.50	91.67	199.90
0.40	59.5	0.6185	25.61	81.52	113.80	204.50

Table 2. Stability constants of Cd (II)-gluconate ion complexes in aqueous & aqueous–alkanol mixtures at 30°C.

Cd (II) = 0.5 mM μ = 0.5

Solvent	Percentage (By volume)	Stability constants β_1	β_2	β_3	β_4
Water	—	16.0	32.0	200.0	—
Methanol	20	10.0	45.0	590.0	—
	40	40.0	240.0	2250.0	—
Ethanol	20	20.0	45.0	955.0	—
	40	15.0	40.0	3450.0	—
Propanol–1	20	25.0	120.0	960.0	—
	40	30.0	130.0	750 0	5750.0

(b) Cd (II)–gluconate ion systems in aqueous alkanol mixtures :

The measurements have been carried out in 20% and 40% alkanol mixtures as precipitation occurs in 60% aqueous-alkanol mixtures.

(i) **in aqueous–methanol mixtures.** The values of the overall formation constants are presented in Table 2.

(ii) **in aqueous–ethanol mixtures.** Three complexes are formed. The overall formation constants are presented in Table 2.

(iii) **in aqueous–propanol–1 mixtures.** In this case also three complexes are formed in 20% aqueous–propanol–1 mixtures and four complexes in 40% aqueous-propanol-1 mixtures. A survey of the formation constants shows that : (i) The stability constants have higher values in aqueous–alkanol

mixtures than in aqueous medium. (ii) The values of the stability constants increase with the increase in the concentration of the alkanols in the aqueous-alkanol mixtures.

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