INDIRECT POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANTS

V. Zinc Complexes of Glycollic and Lactic Acids

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ABSTRACT

Zinc complexes of glycollic and lactic acids were studied by an indirect polarographic method using cadmium as the indicator ion. The half-wave potentials of cadmium complexes shift to more positive values in the presence of zinc. From this shift, the formation function, $\bar{n}$, for zinc was obtained as a function of ligand concentration and the stability constants were calculated.

INTRODUCTION

INDIRECT polarographic method using an indicator ion was first suggested by Ringbom and Eriksson[1] for the study of complexes which are either irreversibly reduced or not even reduced at the dropping mercury electrode. This method appears promising and has not been applied to many systems. Kivalo and Luoto[2] investigated the chloro complexes of zinc and nickel. The stability constants for the cobalt complexes with acetate and propionate have been evaluated by Tedesco and De Rumi.[3] A number of systems[4, 5] have been studied by this method in these laboratories. This paper reports a study of the glycollate and lactate complexes of zinc by the indirect method using cadmium as the indicator ion.

EXPERIMENTAL

Polarograms were obtained at $30 \pm 0{\cdot}5^{\circ}$ C on a manual set-up employing a saturated calomel electrode (S.C.E.) as the reference electrode. The capillary characteristics were: $m = 2{\cdot}05$ mg./sec.$^{-1}$ and $T = 3{\cdot}6$ sec. (in the supporting electrolyte, open circuit). The reported currents have been corrected for the residual currents. Stock solutions of cadmium and zinc, prepared from E. Merck G.R. grade chemicals, were estimated by standard methods. Potassium nitrate (B.D.H., AnalaR), lactic acid (V/o Sojuz Chimexport, Moscow) and glycollic acid (Riedel De HaenAG Seelze-Hannover) were used without further purification. The pH of the solutions

was adjusted with sodium or potassium hydroxide using a Beckman Expandomatic SS–2 pH meter.

Results and Discussion

Cadmium lactate and glycollate complexes undergo reversible reduction, the potentials being more positive than those of the zinc complexes. Hence cadmium was used as the indicator ion in these studies.

Zinc-lactate complexes.—Polarograms of cadmium obtained at different concentrations of lactic acid at pH 6 indicated the reduction to be reversible. The concentration of lactate ion was calculated from the pH of the solution and the pK value of 3·62.[6] The half-wave potentials obtained as a function of lactate concentration (Table I) were used for the evaluation of the stability

Table I

Half-wave potentials of cadmium in lactate medium

$Cd = 4 \times 10^{-4}$ M $\mu = 0{\cdot}5$ (potassium nitrate)

pA	$E_{\frac{1}{2}}$ —V *vs.* S.C.E.	i_d μA	Slope mV
1·70	0·5794	3·30	31·5
1·40	0·5825	3·27	32·5
1·13	0·5890	3·05	32·0
0·89	0·5940	2·90	32·0
0·60	0·6062	2·98	32·5
0·40	0·6160	2·90	32·5
0·30	0·6237	2·79	32·0
0·10	0·6329	2·38	31·5
−0·08	0·6460	2·23	32·0
−0·12	0·6505	2·11	31·5

$E_{\frac{1}{2}\,(s)} = -0{\cdot}5745$ V *vs.* S.C.E., $i_{d\,(s)} = 3{\cdot}22\,\mu$A.

$\beta_1 = 18$; $\beta_2 = 74$; $\beta_3 = 126$.

$\beta_1 = 16$ $\beta_2 = 120$; $\beta_3 = 190$ (ref. 8).

constants by the method of DeFord and Hume.[7] These values were in good agreement with those reported by Thun *et al.*[8] using a quinhydrone electrode.

Polarograms of cadmium in lactate medium were shifted to more positive potentials (Fig. 1) in the presence of zinc due to a decrease in the free ligand concentration. The concentration of the ligand bound to zinc can

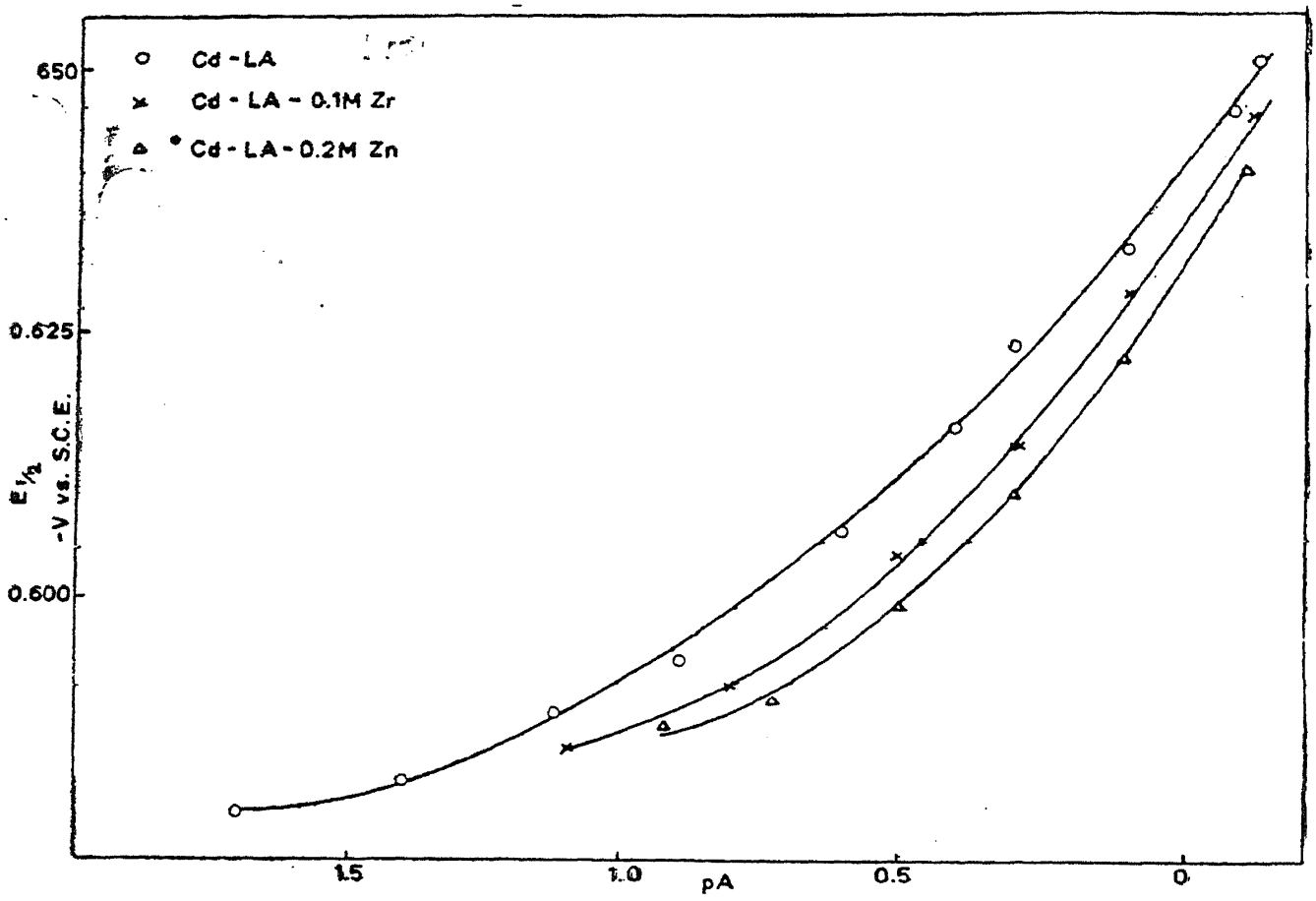

FIG. 1. $E_{1/2}$ *vs.* *p*A in lactate medium

be obtained from the shift in the half-wave potential for the calculation of the Bjerrum's function, $\bar{n}$, defined as[9]

$$\bar{n} = \frac{\text{Conc. of ligand bound to metal}}{\text{Total conc. of metal}}$$

$$= \frac{C_A - [A]}{C_M} \qquad (1)$$

where C_A and C_M are the total concentrations of the ligand and metal respectively and [A] is the free ligand concentration. The $\bar{n}$ function can be expressed in terms of the stability constants, β's, as

$$\bar{n} = (1 - \bar{n})\,\beta_1\,[A] + (2 - \bar{n})\,\beta_2\,[A]^2 + (3 - \bar{n})\,\beta_3\,[A]^3 + \ldots \qquad (2)$$

from which the stability constants can be calculated by the graphical method of Rossotti and Rossotti.[10] The values of $\bar{n}$ calculated at 0·1 and 0·2 M zinc are given in Fig. 2. The stability constants obtained from the graphical plots (Fig. 2) are $\beta_1 = 4{\cdot}5$ and $\beta_2 = 14{\cdot}4$.

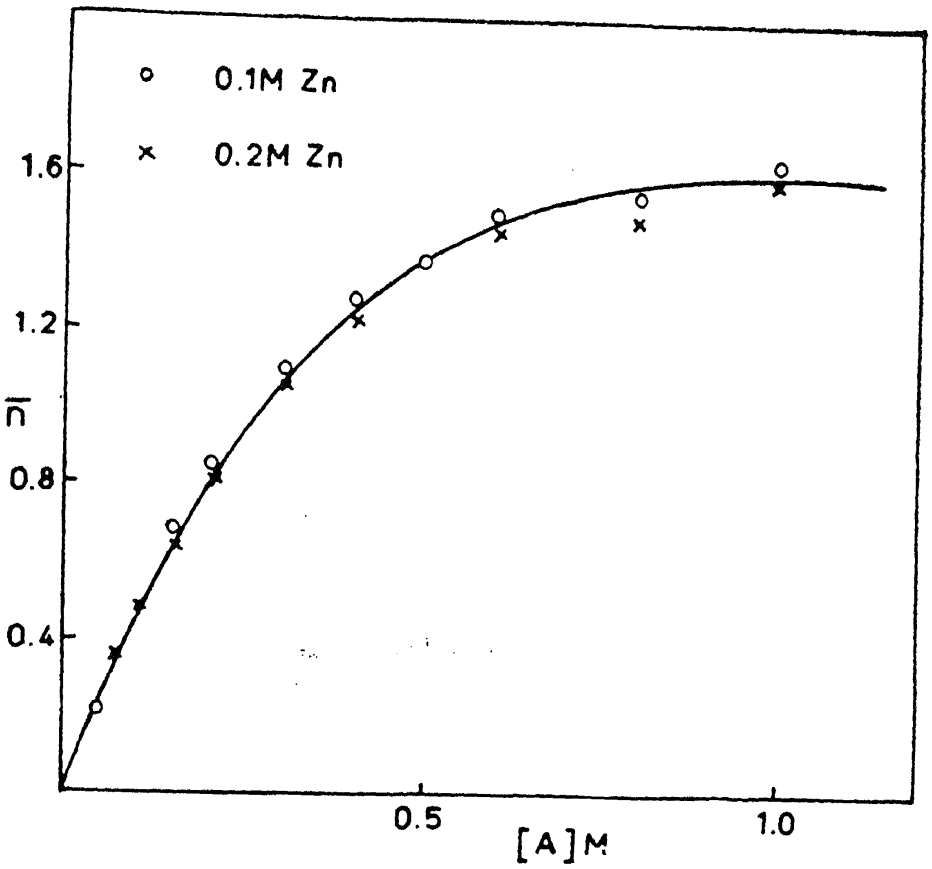

FIG. 2. $\bar{n}$ *vs.* [A] for zinc lactate.

It is also possible to transform the $\bar{n}$ functions to the Fronaeus function, F_0, given by[11]

$$F_0(A) = 1 + \beta_1 [A] + \beta_2 [A]^2 + \beta_3 [A]^3 + \ldots \tag{3}$$

from

$$\partial ln F_0(A) = \bar{n} \,.\, \partial ln [A]. \tag{4}$$

Integrating this expression, we get

$$\log F_0(A) = \int \bar{n} \,.\, \partial \log [A]. \tag{5}$$

The F_0 functions were calculated by a graphical integration (Fig. 3) of the plot of $\bar{n}$ *vs.* log [A]. The stability constants obtained by the graphical method are $\beta_1 = 4{\cdot}8$ and $\beta_2 = 14{\cdot}0$ compared to the values of $\beta_1 = 41$, $\beta_2 = 708$ and $\beta_3 = 1400$ reported by Thun *et al.* It is difficult to explain

this discrepancy in view of the consistency of the $\bar{n}$ values obtained at two different concentrations of zinc.

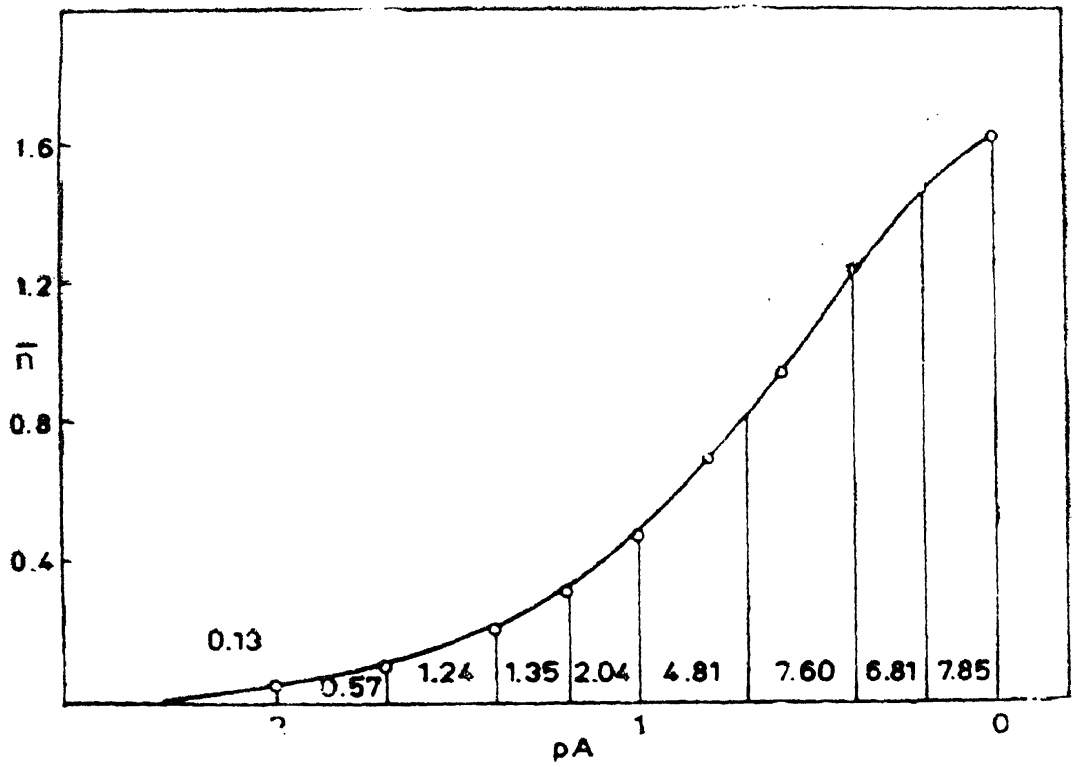

FIG. 3. F_0 (A) from $\bar{n}$ for zinc lactate.

Zinc-glycollate complexes. — The glycollate complexes of zinc were studied in a similar manner. Reversible polarographic waves were obtained for cadmium in glycollate medium (Table II) and the stability constants were calculated graphically by the method of DeFord and Hume. The half-wave potentials of cadmium in glycollate medium were measured (Fig. 4) in the presence of different concentrations of zinc. The values of $\bar{n}$ as well as the F_0 function calculated in a similar manner explained earlier were analysed for the stability constants: $\log \beta_1 = 1{\cdot}46$, $\log \beta_2 = 2{\cdot}65$, $\log \beta_3 = 3{\cdot}05$ and $\log \beta_4 = 3{\cdot}23$. These values were slightly lower compared to those reported by Filipovic *et al.*[12] by a direct polarographic method. It was found that the half-wave potentials calculated from the present values of the stability constants were about 5 mV more positive to those reported by them. A small overvoltage would have led to higher values had the waves not been perfectly reversible.

TABLE II. *Half-wave potentials of cadmium in glycollate medium*

	$\frac{1}{2}$pA	E —V *vs.* S.C.E.	Slope mV
	1·32	0·5925	32·0
	1·03	0·6040	32·5
	0·84	0·6082	32·5
	0·72	0·6150	32·0
	0·54	0·6233	32·5
	0·42	0·6310	32·0
	0·30	0·6360	32·0
	0·22	0·6402	32·0
	0·15	0·6433	32·5

$\beta_1 = 40$; $\beta_2 = 340$.

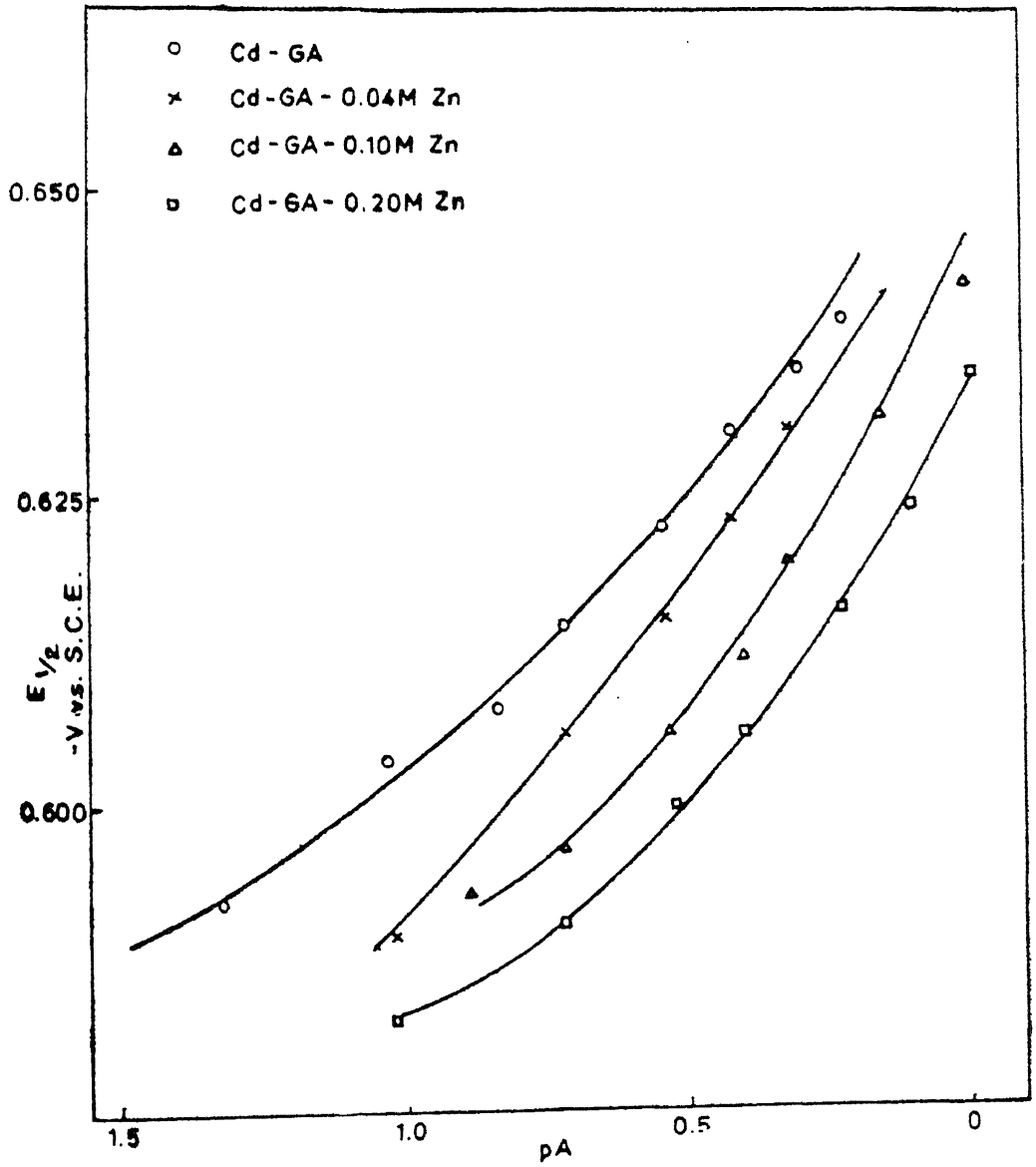

FIG. 4. $E_{1/2}$ *vs.* pA in glycollate medium.

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