INDIRECT POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANTS

II. Pyridine Complexes

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Abstract

Polarograms of cadmium at different concentrations of pyridine were taken in 0·5 M potassium nitrate medium. From a plot of the half-wave potential *vs.* log (Py), the co-ordination numbers of the complexes were calculated to be one and two. The indirect method was applied to the study of cobalt complexes of pyridine. From the shift in the half-wave potentials of cadmium in the presence of cobalt, a plot of $\bar{n}$ *vs.* pA was obtained which indicated the presence of higher complexes of cobalt and pyridine. The stability constants were calculated.

Introduction

In continuation of our work on the study of complexes, an attempt was made to apply the indirect method (Saraiya and Sundaram, 1967) to the study of pyridine complexes.

Experimental

A manual set-up was used for the measurement of current-potential curves. All experiments were carried out in potassium nitrate medium at 30° C., the ionic strength being maintained at 0·5.

Stock solutions of cadmium sulphate (E. Merck) and cadmium nitrate (E. Merck) were standardised gravimetrically. Pyridine (B.D.H. AnalaR) was standardised by titrating against standard hydrochloric acid.

Results and Discussion

Cadmium was chosen as the indicator ion for the study of pyridine complexes by this method. The half-wave potentials, required for reference, were therefore determined under the present experimental conditions.

Polarograms of 0·26 mM cadmium were taken at different concentrations of pyridine in a supporting electrolyte of 0·5 M potassium nitrate. The half-wave potentials at different concentrations of pyridine are represented in Fig. 1 A. The co-ordination numbers were calculated to be one and two from the two straight lines obtained.

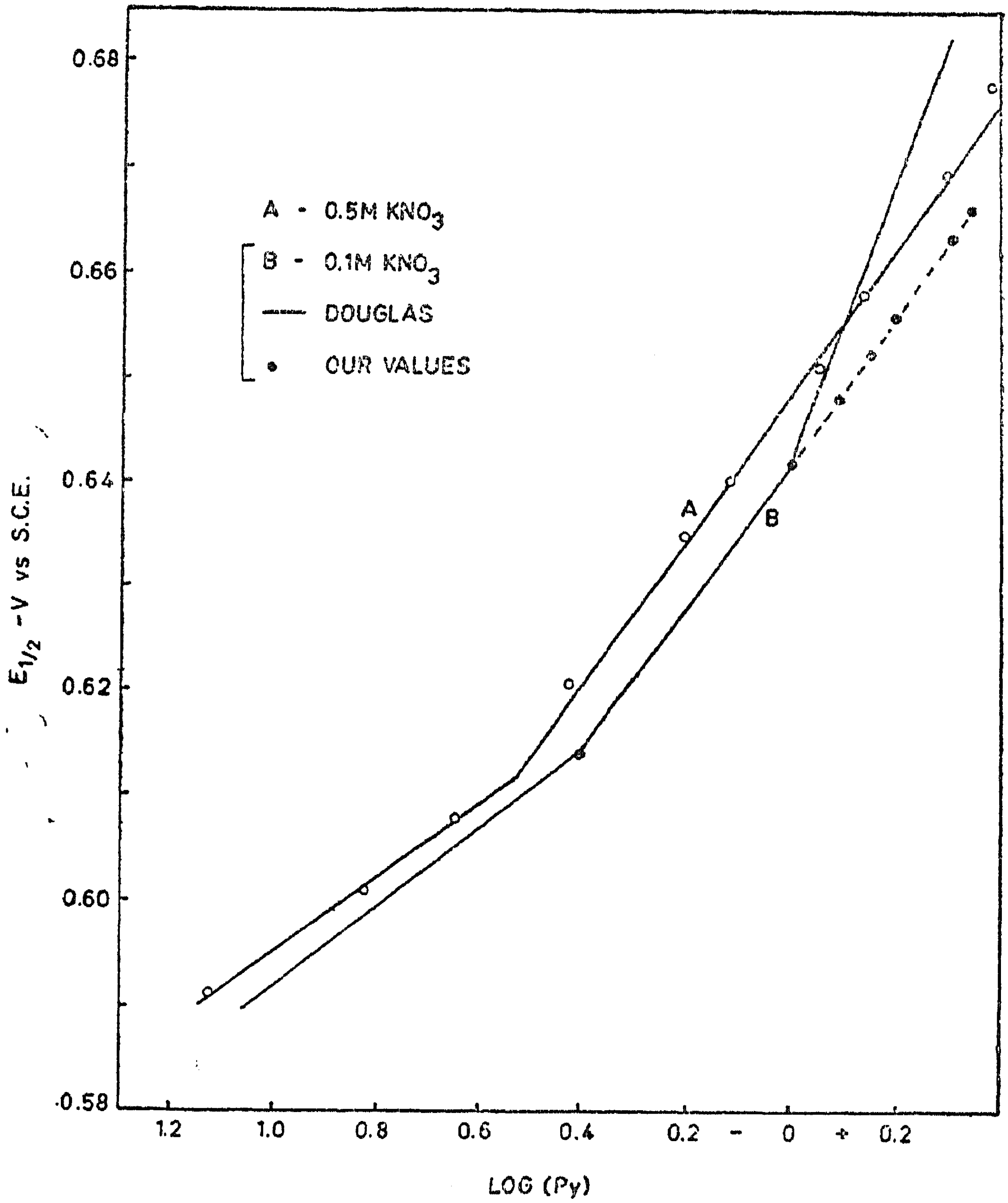

FIG. 1. Plot of $E_{1/2}$ *vs.* log (Py).

Douglas *et al.* (1950) measured the half-wave potentials of cadmium in pyridine medium in 0·1 M potassium nitrate. Their values are represented in Fig. 1 B. In view of the three straight lines observed in their plot, the half-wave potentials were measured by us in the same medium using both cadmium sulphate and nitrate. It can be seen from our results (Fig. 1 B) that two parallel straight lines were obtained at the two concentrations of potassium nitrate. Further experiments at higher concentrations of pyridine up to 5 M indicated only the presence of the second species. The existence of Cd $(Py)_4^{++}$ suggested by earlier workers at concentrations of 1–2 M pyridine appears therefore not justifiable. The stability constants in 0·5 M potassium nitrate for Cd $(Py)^{++}$ and Cd $(Py)_2^{++}$ are $10^{1 \cdot 50}$ and $10^{2 \cdot 25}$ respectively.

An attempt was made to study the pyridine complexes of different metals by the indirect method. No work was carried out with zinc, thorium and lead as a precipitate was obtained. Homogeneous solutions were obtained with nickel, calcium a ndcobalt but in the case of nickel and calcium, even at a metal ion concentration of about 0·2M, no shift in the half-wave potential of cadmium ion was observed indicating that no complexes were formed. A study of cobalt-pyridine complexes was undertaken.

Polarograms of solutions containing cadmium and 0·16 M cobalt were taken at different concentrations of pyridine. The half-wave potentials are represented in Fig. 2 as a function of log (Py). The values of $\bar{n}$ and (A) were

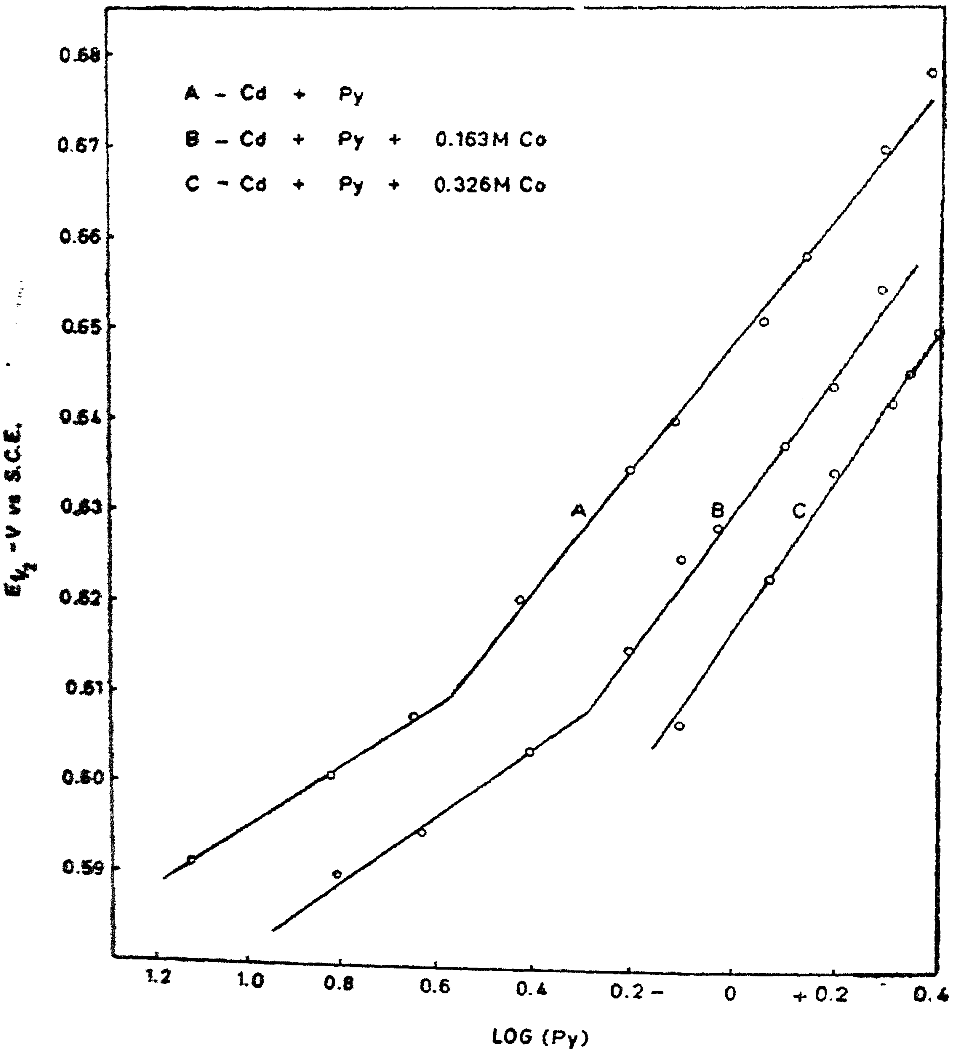

FIG. 2. Plot of $E_{1/2}$ *vs.* log (Py).

calculated from the shift in the half-wave potentials obtained in the presence of cobalt. The results were also checked at 0·32 M cobalt and the $\bar{n}$ values calculated at the two concentrations agreed well.

A plot (Fig. 3) of $\bar{n}$ *vs.* (A) indicated the presence of higher complexes of cobalt and pyridine. The existence of higher complexes was proved by Katzin and co-workers (1950) who prepared Co (Py)$_6$ (NO$_3$)$_2$ and also Co (Py)$_n$ (ClO$_4$)$_2$, where $n = 6$, 7 and 9.

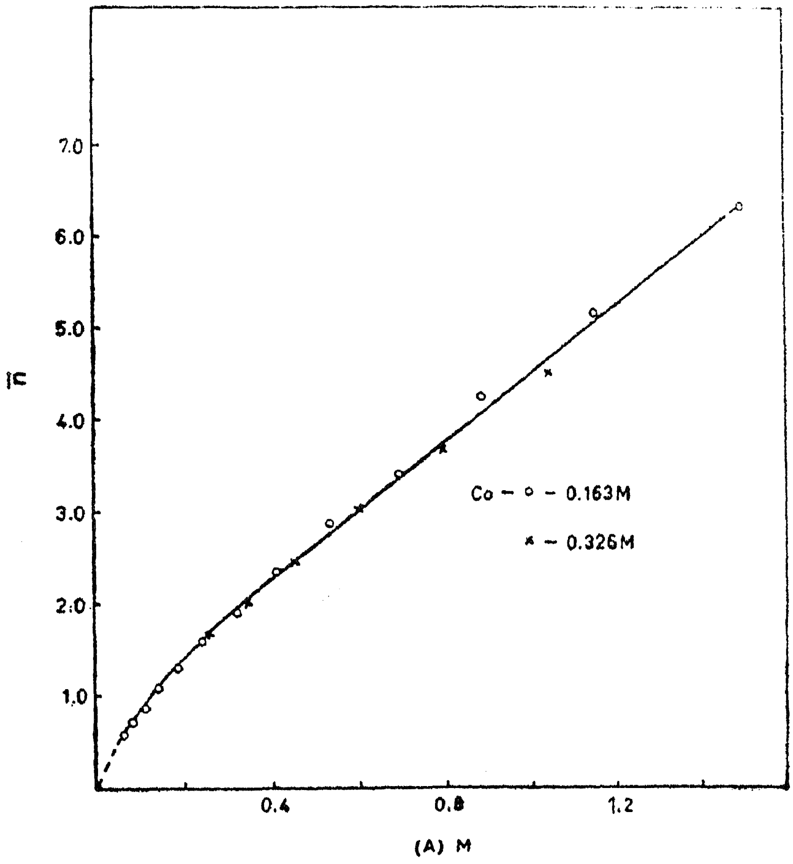

FIG. 3. Plot of $\bar{n}$ *vs.* (A).

The values of $\bar{n}$ *vs.* (A) in Fig. 3 were utilised for the calculation of the stability constants by the method of Rossotti (1955). The plots are given in Figs. 4 and 5 and the values of the stability constants are $\beta_1 = 12 \cdot 5$, $\beta_2 = 30$, $\beta_3 = 82$, $\beta_4 = 90$ and $\beta_5 = 30$. Though the presence of complexes higher than Co (Py)$_5^{++}$ was indicated, no attempt was made to calculate the values because of the low stability of these complexes. A good agreement between the calculated and experimental values of $\bar{n}$ (Table I) was seen up to a pyridine concentration of 0·5 M. Above this, the calculated values were lower than the experimental values as the influence of higher complexes was not taken into consideration.

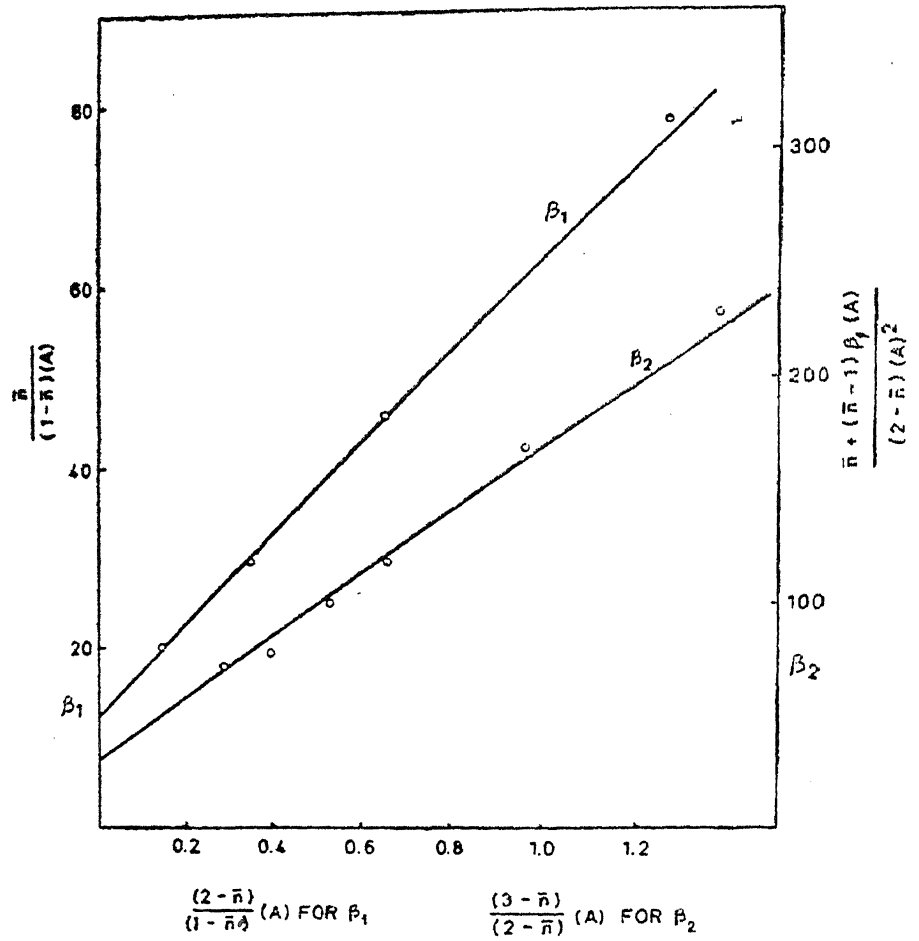

FIG. 4. Rossotti's plots for β_1 and β_2.

TABLE I

Experimental and calculated $\bar{n}$ values

(A)	$\bar{n}$* (calcd.)	$\bar{n}$ (exptal.)
0·10	0·81	0·82
0·14	1·04	1·10
0·20	1·36	1·40
0·25	1·60	1·65
0·30	1·91	1·87
0·40	2·20	2·28
0·50	2·51	2·65
0·60	2·76	3·03

*$\beta_1 = 12·5$; $\beta_2 = 30$; $\beta_3 = 82$; $\beta_4 = 90$; $\beta_5 = 30$.

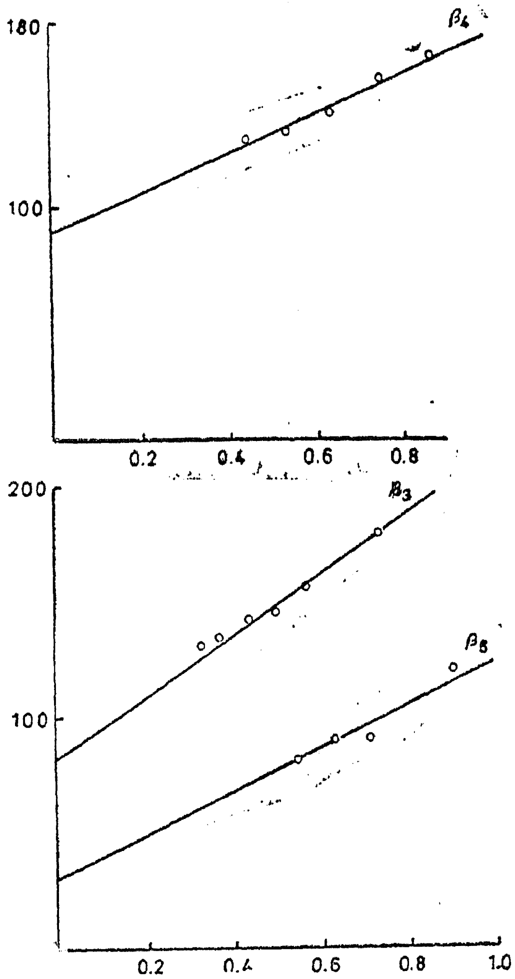

FIG. 5. Rossotti's plots for β_3, β_4 and β_5.

$$\beta_3 : \frac{\bar{n} + (\bar{n} - 1)\beta_1(\mathrm{A}) + (\bar{n} - 2)\beta_2(\mathrm{A})^2}{(3 - \bar{n})(\mathrm{A})^3} \ vs. \ \frac{(4 - \bar{n})\mathrm{A}}{(3 - \bar{n})}$$

$$\beta_4 : \frac{\bar{n} + (\bar{n} - 1)\beta_1(\mathrm{A}) + \ldots + (\bar{n} - 3)\beta_3(\mathrm{A})^3}{(4 - \bar{n})(\mathrm{A})^4} \ vs. \ \frac{(5 - \bar{n})(\mathrm{A})}{(4 - \bar{n})}$$

$$\beta_5 : \frac{\bar{n} + (\bar{n} - 1)\beta_1(\mathrm{A}) + \ldots + (\bar{n} - 4)\beta_4(\mathrm{A})^4}{(5 - \bar{n})(\mathrm{A})^5} \ vs. \ \frac{(6 - \bar{n})\mathrm{A}}{(5 - \bar{n})}.$$

Muftakhov and Dulova (1962) have determined the instability constants of cobalt-pyridine-chloro complexes from spectrophotometric measurements and the values are: $\mathrm{Co(Py)^{++}} = 0{\cdot}049$, $\mathrm{Co\,(Py)_2^{++}} = 0{\cdot}156$ and $\mathrm{Co(Py)_3^{++}} = 0{\cdot}19$. The values obtained by us in 0·5 M potassium nitrate medium are $k_1 = 0{\cdot}08$, $k_2 = 0{\cdot}42$, $k_3 = 0{\cdot}33$, $k_4 = 0{\cdot}9$ and $k_5 = 3{\cdot}3$.

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