Monatshefte für Chemie 108, 361—366 (1977)

Monatshefte für Chemie

Polarographic Studies of Indium(III) Complexes with Some Disubstituted Pyridines

By

R. S. Sindhu, K. B. Pandeya, and R. P. Singh

Department of Chemistry, University of Delhi, Delhi, India

With 4 Figures

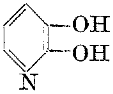
(Received March 4, 1976;
revised July 20, 1976)

Complex formation of indium(III) with three disubstituted pyridines, viz., 2,3-dihydroxypyridine, 2-amino-3-hydroxypyridine and 3-hydroxypyridine-2-thiol has been studied polarographically ($\mu = 0.1$; temp. $= 25 \pm 0.1$ °C). All the systems show reversible electrode behaviour. *DeFord* and *Hume* method as modified by *Irving* has been applied for determining composition and stability constants. Distribution of different species as a function of ligand concentration has been calculated and shown graphically.

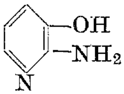
Introduction

Polarography for the study of indium(III) complexes, has been used mainly recently[1–10].

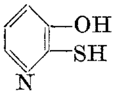
The present paper describes polarographic studies of complex formation of indium with 2,3-dihydroxypyridine (*DHP*) I, 2-amino-3-hydroxypyridine (*AHP*) II and 3-hydroxypyridine-2-thiol (*HPT*) (III),



(I)



(II)



(III)

which form a set of chelating agents containing a phenolic group in combination with three different donor groups. Potentiometric and spectrophotometric studies of some metal complexes with these ligands have been carried out earlier[11].

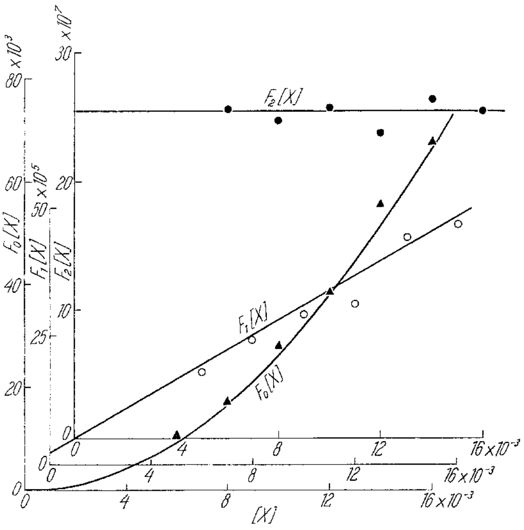


Fig. 1. $F_j[X]$, vs. $[X]$; In(III)—*DHP* system

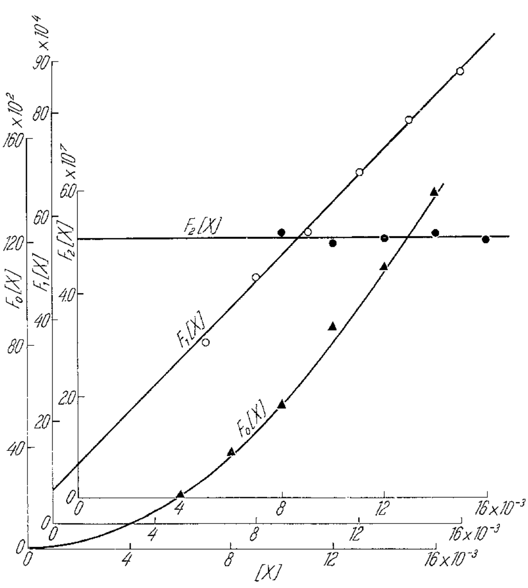


Fig. 2. $F_j[X]$, vs. $[X]$; In(III)—*AHP* system

Experimental

A D.C. manual polarograph with a scalamp galvanometer was used in all investigations. All potential measurements were made with respect to a saturated calomel electrode. The dropping mercury electrode had the characteristics $m^{2/3} t^{1/6} = 2.054\,\mathrm{mg}^{2/3}\,\mathrm{sec}^{-1/2}$, $h = 40$ cm. Purified nitrogen was passed through each solution. All measurements were carried out at 25 ± 0.1 °C.

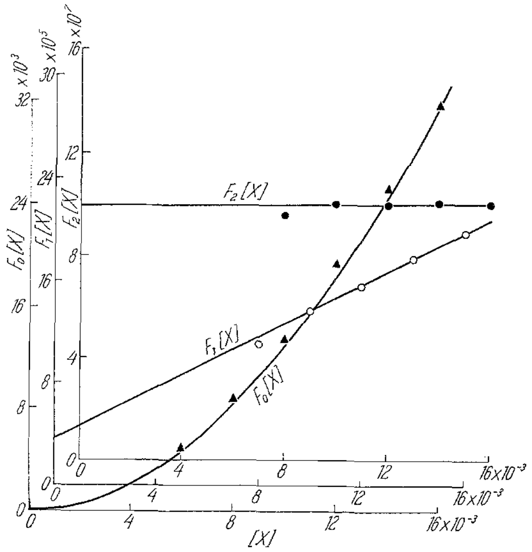


Fig. 3. $F_j\,[X]$, vs. $[X]$; In(III)—*HPT* system

Reagent grade chemicals were used. $InCl_3$ was dissolved in double distilled water. Stock solutions of *DHP* and *AHP* were prepared in double distilled water and that of *HPT* in distilled methanol. While In(III)—*DHP* and In(III)—*AHP* systems were studied in aqueous medium, In(III)—*HPT* system was studied in 40% methanol medium, owing to limited solubility of the ligand in water.

Results and Discussion

The reduction of In(III) in all the three ligands gives single well-defined waves having slopes of log plots, 21 ± 1 mV and $E_{3/4} - E_{1/4}$ values, 19 ± 1 mV, showing that the systems undergo reversible three elecctron reduction. Also the waves in all these three cases are diffusion-controlled as indicated by constancy of $i_d/(h_{\mathrm{eff}})^{1/2}$. With increasing ligand concentration $E_{1/2}$ shifts to more negative potentials, showing complex formation. Plots of $E_{1/2}$ vs. $\log C_x$ (total ligand concentration) yield smooth curves in each case showing the presence of two or more species which are in equilibrium. *DeFord* and *Hume* treatment[12] as modified by *Irving*[13] has been applied for

Table 1. *In(III)—DHP-System* $[In^{3+}] = 1 \times 10^{-4} M$, $\mu = 0.1$ (KCl). Temp. = 25 ± 1 °C; Gelatin = 0.005%; pH = 3.8

$[DHP]$ (m Mole)	$\Delta E_{1/2}$, V	$\log \frac{I_M}{I_C}$	$F_0[X]$ $\times 10^3$	$F_1[X]$ $\times 10^5$	$F_2[X]$ $\times 10^7$
6	0.0730	0.0348	5.493	—	—
8	0.0770	0.0470	9.012	11.264	9.510
10	0.0800	0.0726	13.570	13.569	9.919
12	0.0830	0.0792	19.560	15.466	9.847
14	0.0850	0.0825	24.909	17.790	10.010
16	0.0870	0.0825	31.460	19.660	10.000

$\beta_1 = 3.65 \times 10^5$; $\beta_2 = 9.95 \times 10^7$.

Table 2. *In(III)—AHP-System* $[In^{3+}] = 1 \times 10^{-4} M$, $\mu = 0.1$ (KCl). Temp. = 25 ± 0.1 °C; Gelatin = 0.005%; pH = 5.9

$[AHP]$ (m Mole)	$\Delta E_{1/2}$, V	$\log \frac{I_M}{I_C}$	$F_0[X]$ $\times 10^2$	$F_1[X]$ $\times 10^4$	$F_2[X]$ $\times 10^7$
6	0.0650	0.0288	21.26	35.410	4.776
8	0.0700	0.0348	38.67	48.610	5.23
10	0.0730	0.0470	56.46	56.450	4.970
12	0.0760	0.0533	87.34	67.775	5.08
14	0.0785	0.0596	110.50	78.92	5.15
16	0.0805	0.0596	139.60	87.25	5.03

$\beta_1 = 6.75 \times 10^4$; $\beta_2 = 5.09 \times 10^7$.

Table 3. *In(III)—HPT-System* $[In^{3+}] = 1 \times 10^{-4} M$, $\mu = 0.1$ (KCl). Temp. = 25 ± 0.1 °C; Gelatin = 0.05%; pH = 3.8

$[HPT]$ [m Mole)	$\Delta E_{1/2}$, V	$\log \frac{I_M}{I_C}$	$F_0[X]$ $\times 10^3$	$F_1[X]$ $= 10^5$	$F_2[X]$ $\times 10^7$
6	0.078	0.0726	10.74	17.88	25.63
8	0.082	0.0860	17.68	22.10	24.50
10	0.0855	0.0928	27.67	27.67	25.17
12	0.090	0.0997	36.94	30.79	23.58
14	0.0915	0.0997	55.38	39.55	26.40
16	0.0930	0.1176	68.77	42.98	25.30

$\beta_1 = 2.5 \times 10^5$; $\beta_2 = 25.4 \times 10^7$.

analysis of the results (Tables 1, 2, and 3). The formation constants have been obtained from $F_{0-j}[X]$ vs. ligand concentrations curves (Figs. 1, 2, and 3). Since plots of $F_1[X]$ and $F_2[X]$ show a sloped and a horizontal straight lines, respectively, only 1 : 1 and 1 : 2 metal to ligand species are formed.

A perusal of the formation constant data for the three systems show that $K_1 > K_2$, as also expected owing to steric and statistical considerations.

In^{3+} is a class "a" acceptor. Strength of metal—donor bond for In(III) complexes is, therefore, expected to follow the order $O > N > S$. The three ligands under study contain respectively phenolic (*DHP*), amino (*AHP*) and thiol (*HPT*) groups ortho to a phenolic group. The stability of the In(III) complexes with these ligands are, thus, expected to follow the order *DHP* > *AHP* > *HPT*. The same is found also to be true for *DHP* and *AHP* where studies have been made in similar conditions. Due to smaller dielectric constant value of 40% methanol the stability of In(III) — *HPT* in this medium may get enhanced[14]. This may be responsible for high value of stability constant found for In(III) — *HPT* complex.

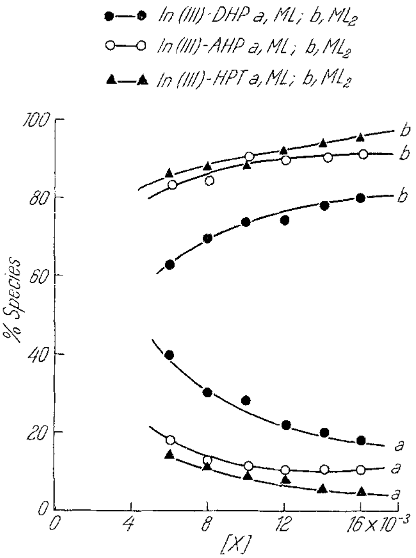


Fig. 4. Distribution of complex species as a function of ligand concentration

The proportion of the uncomplexed metal ion and the various complex species as a function of the ligand concentration has been calculated by means of the equations

$$\frac{M}{C_M} = \frac{1}{F_0[X]} \tag{1}$$

$$\frac{MX_j}{C_M} = \frac{\beta_j [X]^j}{F_0[X]} \tag{2}$$

where M denotes the concentration of the uncomplexed metal ions, MX_j is the concentration of the jth complex and C_M is the total metal ion concentration added to the system. The percentage distribution of the species as a function of ligand concentration is shown in Fig. 4.

Acknowledgement

One of the authors (*R. S. S.*) is thankful to the Council of Scientific and Industrial Research, New Delhi for award of a Junior Research Fellowship.

References

[1] *D. Cozzi* and *S. Vivarelli*, Z. Elektrochem. **58**, 907 (1954).
[2] *P. C. Rawat* and *C. M. Gupta*, Talanta **19**, 706 (1972).
[3] *A. V. Pandeya* and *M. L. Mittal*, J. Inorg. Nucl. Chem. **34**, 2365 (1972).
[4] *L. Treindl*, Rev. Chim. Miner. **5**, 397 (1968).
[5] *J. J. Savič* and *I. Filipovič*, Croat. Chem. Acta **37**, 91 (1965).
[6] *V. F. Toropova*, *G. K. Budnikov*, *V. N. Maistrenko*, and *I. V. Nagorskova*, J. Gen. Chem. of U.S.S.R. **43**, 2117 (1973).
[7] *Ya. I. Tur'yan* and *N. K. Strizhov*, Russ. J. Inorg. Chem. **17**, 1066 (1972).
[8] *R. S. Saxena* and *U. S. Chaturvedi*, J. Inorg. Nucl. Chem. **34**, 3272 (1972).
[9] *J. N. Gaur*, *D. S. Jain*, and *M. M. Palrecha*, J. Chem. Soc. A **1968**, 2201.
[10] *J. N. Gaur*, *R. C. Mehrotra*, *M. M. Palrecha*, *D. S. Jain*, *Anand Kumar*, and *C. M. Gupta*, J. Polarogr. Soc. **14**, 122 (1968).
[11] *Veena Kushwaha*, *M. Katyal*, and *R. P. Singh*, Talanta **21**, 763 (1974).
[12] *D. D. DeFord* and *D. N. Hume*, J. Amer. Chem. Soc. **73**, 5321 (1951).
[13] *H. Irving*, Advances in polarography **1**, 42 (1960).
[14] *Y. I. Turyan* and *N. L. Bondarenko*, Zh. neorg. Khim. **4**, 1070 (1959).

Correspondence and reprints:
Dr. K. B. Pandeya
Department of Chemistry
University of Delhi
IND-110 007 Delhi-7
India